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Combinatorial experimental and DFT theoretical investigation over the formation mechanism of a binuclear phthalocyanine dimer†

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Herein, a density functional calculation method was used to explore the formation mechanism of a metal-free, homobinuclear phthalocyanine dimer. The result not only well rationalizes the Pc dimer formation starting from 1,2-diamino-9,10,16,17,23,24-hexa-(2,6-dimethylphenoxy)-tribenzotetrazaporphyrin (1-OR) through an intricate pathway but, more importantly, also predicts the formation of ammonia during the reaction process; this results in the successful experimental detection of NH₄⁺ in the acidic reaction system. Further experimental efforts have facilitated the isolation of one of the theoretically revealed reaction intermediates di-[2-amino-7,8,14,15,21,22-hexa-(2,6-dimethylphenoxy)-tribenzotetrazaporphyrinato]-amine (9-OR); this indicates the significance of combining experimental with DFT calculation method towards clarifying the reaction mechanisms.

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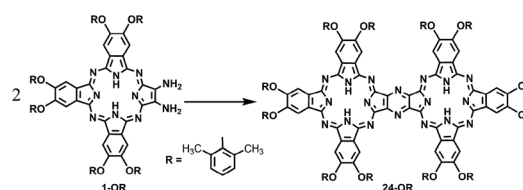
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Introduction

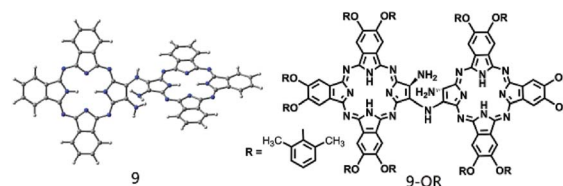
In the past few decades, quantum chemistry, particularly in combination with density functional theory (DFT), has become a remarkable tool for chemists towards understanding the reaction mechanism or designing new type of reactions.¹ First, quantum chemistry enables to elaborately study the modeling elementary reactions on the basis of reactivity and selectivity.² In addition, overall reaction pathways can be elucidated by computational chemistry.³ Unambiguously, a combination of computational investigation and experimental studies can lead to a better understanding of mechanistic details (Schemes 1–3).

On the other hand, phthalocyanines (Pcs) have found a wide range of novel applications as advanced materials in addition to their traditional industrial applications in the past few decades.⁴ For the purpose of developing new Pc-based molecular materials, phthalocyanine oligomers, in particular, phthalocyanine dimers with conjugated electronic structures, have received extensive attention.⁵ Despite the great efforts being paid in this direction, the synthesis, especially the isolation of conjugated phthalocyanine dimers, still remains a significant challenge due to the statistical mixed product

obtained from the random cyclotetramerization of 1,2,4,5-tetracyanobenzene with a second phthalonitrile, as shown in Scheme S1 (ESI†).⁶ However, recently, a novel post-cyclotetramerization strategy towards the efficient synthesis of binuclear Pcs in an impressively high yield under very mild reaction conditions has been developed by Jiang *et al.*⁷ For further extending the potential of this newly developed method to the synthesis of novel conjugated Pc oligomers, insight into



Scheme 1 Schematic showing the synthesis of the metal-free homobinuclear phthalocyanine 24-OR in CH₂Cl₂ at room temperature in the mixed solvent of CH₂Cl₂ and TFA (in the ratio of 80 : 20), with 1-OR as the starting reagent.



Scheme 2 Schematic of the molecular structures of the relatively stable di-tribenzotetrazaporphyrinato-amine intermediates 9 and (9-OR).

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Fig. 2 Energy profile for the dehydrogenation of intermediate **9**, along with the relative energies.

with a high energy barrier of $38.16 \text{ kcal mol}^{-1}$, which is surely thermodynamically unfavorable. On the other hand, the formation of the final product can be facilitated by TFA, which actually also acts as a H-transfer shuttle. As shown in Fig. 3, the concerted H-transfer reaction assisted by TFA, along with the formation of the target dimeric Pc **24** as well as ammonia, with a slight energy barrier of $11.00 \text{ kcal mol}^{-1}$, is undoubtedly favorable under the experimental condition. Actually, the effect of the shuttle can be easily understood: TFA can transfer the two hydrogen atoms linearly; thus, the elementary reaction *via* the transition state **TS22** is favorable in energy. In contrast, the tension of the four-membered ring in the pericyclic reaction in **TS21'** results in a very large energy barrier.

Reviewing the whole reaction pathway, the crucial catalytic role of TFA for the self-condensation reaction is unambiguously disclosed by the DFT calculation. At the early stage, it is necessary to activate the initial reagent by acid. However, it is worth noting that a very strong acid, such as sulfuric acid or hydrochloric acid, in particular, in excess amount would protonate all the initial reagents; this then prevents the reaction from further proceeding since two protonated reagents cannot react with each other due to electronic repulsion. On the other hand, a weak acid, such as acetic acid or propanoic acid (even in excess amount) is not able to protonate a sufficient amount of the initial reagents to initiate the reaction. Both results are fully

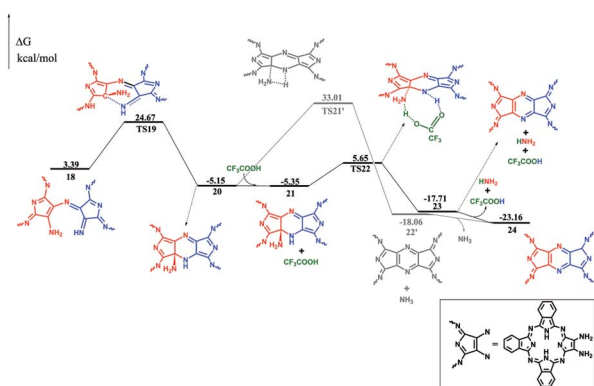


Fig. 3 Energy profile for the formation of the final product **24**, along with the relative energies.

in line with the experimental findings.⁷ As a result, only TFA with suitable acidic intensity and in an appropriate quantity could lead to excellent synthesis result for the binuclear Pcs from 1,2-diamino-9,10,16,17,23,24-hexa-(2,6-dimethylphenoxy)-tribenzotetrazaporphyrin (**1-OR**). Moreover, the two elementary reactions are facilitated by TFA as an H-transfer shuttle. As can be seen in Fig. S4 (ESI[†]), the structure of TFA perfectly fits the hydrogen transfer orientation and thus can significantly decrease the energy barrier. Overall, TFA with appropriate acidity and geometric configuration and in a suitable quantity can act as a good catalyst for this reaction.

To validate the abovementioned reaction mechanism, effort is paid towards the detection of ammonia formed in the reaction system. The reaction mixture was extracted using water. When treated with the Nessler's reagent, the separated aqueous solution turns from light yellow to orange¹⁵ [see Fig. S5 (ESI[†])]; this confirms the existence of NH_4^+ in this acidic reaction system and indicates the production of NH_3 during the formation of **24-OR** in the self-condensation of **1-OR**, corresponding well with the calculation prediction.

However, since DFT calculations also predicted a series of reaction intermediates with relatively good stabilities (as shown by their relatively low Gibbs energies), trials have been carried out to isolate them during the self-condensation reaction of **1-OR** in CH_2Cl_2 and TFA in the ratio of 80 : 20 by monitoring the progress using thin layer chromatography (TLC). TLC monitoring indicated that after the reaction progresses for only 0.5 h, the dimeric phthalocyanine compound **24-OR** starts to appear. In addition, the monomeric phthalocyanine precursor **1-OR** completely disappears after 3 h reaction. However, a new species with green color and larger polarity than the dimeric compound **24-OR** starts to appear 1 h after the reaction starts, which completely disappears after the reaction proceeds for 4 h; this suggests the possible reaction intermediate nature of this newly observed species during the formation procedure of **24-OR**. Fortunately, this compound is isolated from the reaction system after 1.5 h reaction by column chromatography in 13% yield in addition to the unreacted monomeric phthalocyanine precursor **1-OR** and target phthalocyanine dimer **24-OR**. MALDI-TOF in combination with the NMR spectroscopic result, as shown in Fig. S6 and S7 (ESI[†]), reveals the dimeric phthalocyanine nature of this compound, which is actually the monoamine-substituted binuclear phthalocyanine intermediate species **9-OR**, the counterpart of the intermediate **9** shown in Fig. 2. Further support for the intermediate nature of this species originates from the transformation of **9-OR** into the target homo-binuclear phthalocyanine dimer **24-OR** in CH_2Cl_2 and TFA (80 : 20) at room temperature in a yield of 82% after 5 h reaction. This result provides solid experimental validation for the formation mechanism of Pc-dimer, revealed on the basis of DFT calculation.

At the end of this section, it is worth noting that the successful isolation of **9-OR** can also be well rationalized on the basis of the DFT calculations. As shown in Fig. 2, the reaction between the intermediate **9** and the oxygen molecule is an endergonic process, indicating its thermodynamically unfavorable nature. In addition, the intermediate **9** is a thermodynamically stable species (with the reaction exergonicity of $0.87 \text{ kcal mol}^{-1}$ relative to that of the



reactant **1**). Overall, the intermediate **9** would accumulate and therefore is able to be isolated during the reaction process.

Conclusions

In conclusion, the mechanistic details of the formation of a metal-free homo-binuclear phthalocynine dimer by the self-condensation of 1,2-diamino-9,10,16,17,23,24-hexa-(2,6-dimethylphenoxy)-tribenzotetrazaporphyrin have been clarified *via* a combination of experiments and density functional calculations. The appropriate acidity and geometric configuration of TFA play an important role in activating the precursor and acting as an H-transfer shuttle to promote the reaction. The production of ammonia was initially predicted by the theoretical study and then confirmed experimentally. Furthermore, one of the theoretically determined reaction intermediates was successfully isolated during the reaction process; this demonstrated the validity of the theoretical calculation. The present result clearly demonstrates the significance of combining theoretical calculations with experiments.

Experimental detail

Synthesis and isolation of the intermediate **9-OR** in the mixed solvent of CH₂Cl₂ and TFA in the ratio of 80 : 20

Compound **1-OR** (37.7 mg, 0.0310 mmol) was dissolved in 3.0 mL of the mixed solvent of CH₂Cl₂ and TFA in the ratio of 80 : 20 and stirred at room temperature for 1.5 h. The reaction mixture was poured into water (10 mL) and extracted with CH₂Cl₂ (3 × 5 mL). The combined organic solution was then washed with water (3 × 5 mL) and dried with Na₂SO₄/K₂CO₃. After evaporating the solvent, the residue was chromatographed on a silica gel column with CH₂Cl₂ as an eluent to obtain a green band containing the intermediate **9-OR**, and then, another green band containing compound **24-OR** was obtained. Repeated chromatography followed by recrystallization from CH₂Cl₂ and CH₃OH provided the intermediate **9-OR** as a green powder in a yield of 13% (along with **24-OR** in a yield of 36%). ¹H NMR (400 MHz, CDCl₃) for **9-OR** = 9.32 (s, 1H), 8.40 (s, 1H), 8.34 (m, 5H), 8.08 (br, 5H), 7.37 (br, 30H), 7.00–7.06 (m, 6H), 2.25–2.58 (m, 72H), –0.16 ppm (m, 4H); MS (MALDI-TOF): Calcd. For C₁₅₂H₁₂₉N₁₉O₁₂ [M]⁺ 2413.0; found *m/z* 2413.1.

Reaction of the intermediate **9-OR** in the mixed solvent of CH₂Cl₂ and TFA in the ratio of 80 : 20

By employing the abovementioned synthesis procedure of compound **24-OR** in the mixed solvent of CH₂Cl₂ and TFA in the ratio of 80 : 20 with **9-OR** instead of compound **1-OR** as the starting material with the reaction time of 5 h, the compound **24-OR** was isolated in the yield of 82%.

Detection of NH₄⁺ during the formation of **24-OR** from the self-condensation reaction of **1-OR** in the mixed solvent of CH₂Cl₂ and TFA in the ratio of 80 : 20

Compound **1-OR** (62.8 mg, 0.0516 mmol) was dissolved in the mixed solvent of CH₂Cl₂ and TFA in the ratio of 80 : 20 (5.0 mL)

and stirred at room temperature for 5 h. Then, the reaction mixture was poured in water (10 mL) and extracted with CH₂Cl₂ (3 × 5 mL). The combined organic solution was then washed with water (3 × 10 mL). The aqueous phases were combined, and the pH value of the resulting solution adjusted to 7.0 by adding 0.1 M KOH solution. Then, 0.1 mL of the aqueous solution was added to 2 mL Nessler's reagent, and the solution immediately changed from light yellow to orange.

Detection of NH₄⁺ during the formation of **24-OR** from the intermediate **9-OR** in the mixed solvent of CH₂Cl₂ and TFA in the ratio of 80 : 20

The abovementioned detection procedure of NH₄⁺ during the formation of **24-OR** from the self-condensation reaction of **1-OR** in the mixed solvent of CH₂Cl₂ and TFA in the ratio of 80 : 20 with the intermediate **9-OR** instead of compound **1-OR** was employed, and the Nessler's reagent changed from light yellow to orange.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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