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Synergistic *meso*- β regulation of porphyrins: squeezing the band gap into the near-infrared I/II region†

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The development of novel near-infrared (NIR) materials with extremely small energy gaps and high stability is highly desirable in bioimaging and phototherapy. Here we report an effective strategy for narrowing the energy gaps of porphyrins by synergistic regulation of *meso*/ β substituents. The novel NIR absorbing/emitting *meso*-alkynyl naphthoporphyrins (Zn-TNP and Pt-TNP) are synthesized *via* the retro-Diels–Alder reaction. X-ray crystallography analysis confirms the highly distorted structures of the complexes. Both compounds exhibit intense Q bands around 800 nm, while Zn-TNP shows deep NIR fluorescence at 847 nm. Pt-TNP displays NIR-II room temperature phosphorescence peaking at 1106 nm with an extremely large Stokes shift of 314 nm, which are the longest wavelengths observed among the reported platinum porphyrinoids. Furthermore, Pt-TNP shows remarkable photostability and a notable capacity for synchronous singlet oxygen and heat generation under NIR light irradiation, demonstrating potential in combined photodynamic/photothermal therapy. A theoretical analysis reveals the progressive lifting of the HOMO by the β -fused benzene ring, the decrease of the LUMO upon *meso*-alkynyl substitution, and energy-releasing pathways varying with metal ions. This dual regulation approach demonstrates great promise in designing innovative multifunctional NIR porphyrin materials.

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Introduction

Organic near-infrared (NIR) materials are in high demand for bio-imaging and phototherapy due to their great advantages including low cytotoxicity, deep tissue penetration, and minimal damage to normal tissues.^{1–5} As important pigments of life, porphyrinoids can be readily functionalized *via* inner-core coordination and peripheral modifications. The common tetrapyrrolic porphyrins are 18 π aromatic conjugated molecules displaying intense Soret bands and weak Q bands in the visible region, but they lack near-infrared (NIR) absorption. Therefore, considerable effort has been devoted to obtaining NIR-absorbed porphyrinoids by modifying the structure, which narrows the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap. Among various designing strategies, such as developing π -extended,⁶ MO-mixing^{7,8} and

donor–acceptor⁹ systems, pyrrolic β -aromatic-fusion¹⁰ stands out as an exceptional approach for producing rigid porphyrins with intensified Q bands in NIR-absorption and emission. The Q bands of porphyrins can undergo a gradual red-shift by the tetra-fusion of benzene^{11–13} (600–700 nm), naphthalene^{14–16} (700–800 nm), and anthracene^{17–20} (>800 nm), accompanied by a notable intensity increase.²¹ Despite having the longest NIR absorption and emission bands, the anthracene-fused (anthro) porphyrins were easily photooxidized under ambient light,²² which severely restricted their practical uses.

While considerable research has been conducted on expanding the porphyrinoid π -system *via* pyrrolic β -functionalization, little attention has been paid to decreasing the HOMO–LUMO gap by adjusting *meso*-substituents. Most porphyrins have *meso*-aryl substituents, resulting in a minor change in the HOMO–LUMO gap, because both electron-withdrawing and electron-donating groups in phenyl always cause a simultaneous rise or decrease in the HOMO and LUMO. Kobayashi *et al.* reported the design of stable, NIR-absorbing phthalocyanines by rationally controlling both the central core and the α -substituent, demonstrating the efficiency of multipart regulation in energy-gap tuning.^{23–25} *Meso*-alkynyl groups have been incorporated into porphyrinoids²⁶ to facilitate intermolecular coupling and create nanoscale tape and rings^{27–29} with a high degree of conjugation. In this work, combined with π -extension at β -positions, we highlight the additional HOMO–

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LUMO gap narrowing ability of alkynyl groups at *meso* positions (Fig. 1). Upon the *meso*- β double regulation, our newly synthesized *meso*-alkynyl naphthalene-fused (naphtho)porphyrin complexes **Zn-TNP** and **Pt-TNP** demonstrate not only a more pronounced red-shift in both absorption and emission (>800 nm), but also significantly higher photostability than their NIR-absorbing *meso*-aryl anthroporphyrin counterparts. Notably, the platinum coordinated **Pt-TNP** is a rare example of a porphyrinoid emitter that displays phosphorescence in the desirable NIR-II (1000–1400 nm) window with a maximum of 1106 nm at room temperature, while presenting an ultra-large Stokes shift exceeding 300 nm. Furthermore, **Pt-TNP** exhibits significant singlet oxygen generation and photothermal conversion capacity under NIR laser irradiation, making it an ideal agent for multifunctional phototherapy.³⁰

Results and discussion

The synthesis route is presented in Fig. 2a. 4,9-Dihydro-4,9-ethano-2*H*-benz[*f*]isoindole **1** bearing a bicyclo[2.2.2]octadiene (BCOD) unit was synthesized *via* a reported method.³¹ The condensation of **1** and 3-(triisopropylsilyl)propionaldehyde **2** (ref. ³²) was catalyzed by BF₃·OEt₂ in ultra-dry CH₂Cl₂ under an N₂ atmosphere, followed by oxidation with *p*-chloranil (TCQ), and afforded free-base porphyrin **3** in 9% yield.³³ Adding a methanol solution of Zn(OAc)₂ to the CHCl₃ solution of **3** afforded the zinc-coordinated porphyrin **Zn-3** in 93% yield. The platinum complex **Pt-3** was synthesized in 93% yield *via* the reaction between **3** and PtCl₂ in refluxing acetic acid. The naphthoporphyrins **Zn-TNP** and **Pt-TNP** were quantitatively obtained by employing the retro-Diels–Alder method,³⁴ heating precursors **Zn-3** and **Pt-3** in solid states, respectively, at 300 °C under vacuum.

The successful synthesis of the desired fused porphyrins was confirmed by HR-ESI mass spectrometry and MALDI-TOF mass spectrometry (Fig. S1–S10†), and nuclear magnetic resonance (NMR) spectroscopy (Fig. S12–S16†). The resonance signals of protons on the fused naphthalenes of **Zn-TNP** (Fig. 2b) are divided into three groups: H₁ at δ = 10.9 ppm, H₂ at δ = 8.41 ppm and H₃ at δ = 7.75 ppm, which shift more downfield than those of the *meso*-tetraphenyl[2,3]tetranaphthoporphyrin zinc complex (**Zn-TPTNP**) reported by Ito *et al.*^{14,35} The NMR computational simulation of **Zn-TNP** shows consistency with the experimental results, with H₁ at δ = 10.9/11.0 ppm, H₂ at δ =

8.56/8.66 ppm, and H₃ at δ = 7.95/7.97 ppm. To further explain the downfield proton signals on **Zn-TNP**, particularly the significantly shifted H₁, the 3D isochemical shielding surface (ICSS) calculation^{36,37} was performed (Fig. 2c). The overall aromaticity of **Zn-TNP** is indicated by the large shielding area (blue) enclosing the entire molecule. Enhanced deshielding (red) is observed in the area between the alkynyl groups and fused naphthalenes of **Zn-TNP**, which mainly surrounds the H₁ protons. Consequently, the presence of alkynyl groups induces a more significant downfield shift in the signal of H₁, while the signals of H₂ and H₃ also undergo a slight downfield shift.

The solid structures of **Zn-TNP** and **Pt-TNP** were examined using single-crystal X-ray diffraction. The single crystals of **Zn-TNP** were obtained by slow diffusion of hexane into its CH₂Cl₂ solution containing a small amount of Et₄NCl. As a consequence of Cl[−] axial coordination, the Zn–N bond lengths range from 2.072(5) to 2.137(6) Å, which are longer than those of common four-coordinated Zn porphyrins (2.039–2.040 Å).³⁸ The Zn(II) ion is located at 0.384 Å above the 4N plane, and the length of the Zn–Cl bond is 2.335(2) Å. The single crystals of **Pt-TNP** were obtained by slow evaporation of its toluene solution for a month. The bond length of Pt–N is 2.0073(14) Å, which is identical to those of the reported (5,10,15,20-tetraphenyl-21*H*,23*H*-porphinato)platinum(II).³⁹ The bond length alternations in crystal structures are analyzed by the harmonic oscillator model of aromaticity⁴⁰ (HOMA). The HOMA values of **Zn-TNP** and **Pt-TNP** for the 18 π -circuit (containing 16 atoms as a macrocyclic internal cross) are 0.88 and 0.90, respectively, which are typical for aromatic porphyrinoids.⁴¹ **Zn-TNP** and **Pt-TNP** have skeleton lengths of 16.957 Å and 17.179 Å, respectively, determined by the distance between the terminal carbon atoms on the fused naphthalenes (Fig. 3a). Both **Zn-TNP** and **Pt-TNP** exhibit highly distorted conformations, which are further investigated using the clothes-line diagrams (Fig. 3b) and normal-coordinate structural decomposition (NSD) method^{42,43} (Tables S3 and S4†). **Zn-TNP** has a saddled conformation (B_{2u} = 1.89), while **Pt-TNP** has a distinct hybrid conformation that is primarily saddled (B_{2u} = 2.59) and partly ruffled (B_{1u} = 1.15). The single crystal packing structure of **Zn-TNP** displays a wave-shaped extension along the *a* and *c* directions. The formation of the “wave” is constructed by the face-to-face π -stacking between the fused naphthalenes in **Zn-TNP** molecules. And the **Zn-TNP** wave layers are separated by the Et₄N⁺ counterions. The packing structure of **Pt-TNP** is arranged in an interleaved manner, showing slipped π - π interaction of the fused naphthalenes (Fig. 3c).

The absorption, luminescence, and magnetic circular dichroism (MCD) spectra of the new porphyrin compounds were recorded in toluene to investigate the photophysical properties (Fig. 4a and b). The precursors **Zn-3** and **Pt-3** display typical intense Soret bands at 487 and 466 nm, respectively, which are red-shifted in comparison to the Soret band of *meso*-tetraphenylporphyrin at *ca.* 410 nm (Fig. S21 and S22†). The Soret bands of **Zn-TNP** and **Pt-TNP** are further red-shifted to 549 nm and 520 nm, respectively. The Q bands of the **Zn-3** and **Pt-3** are weak and located in the visible region. After naphthalene-fusion, the Q bands of **Zn-TNP** and **Pt-TNP**

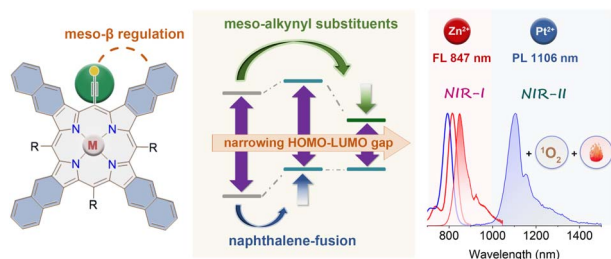


Fig. 1 Molecular design of target NIR-absorbing/emitting porphyrin complexes.



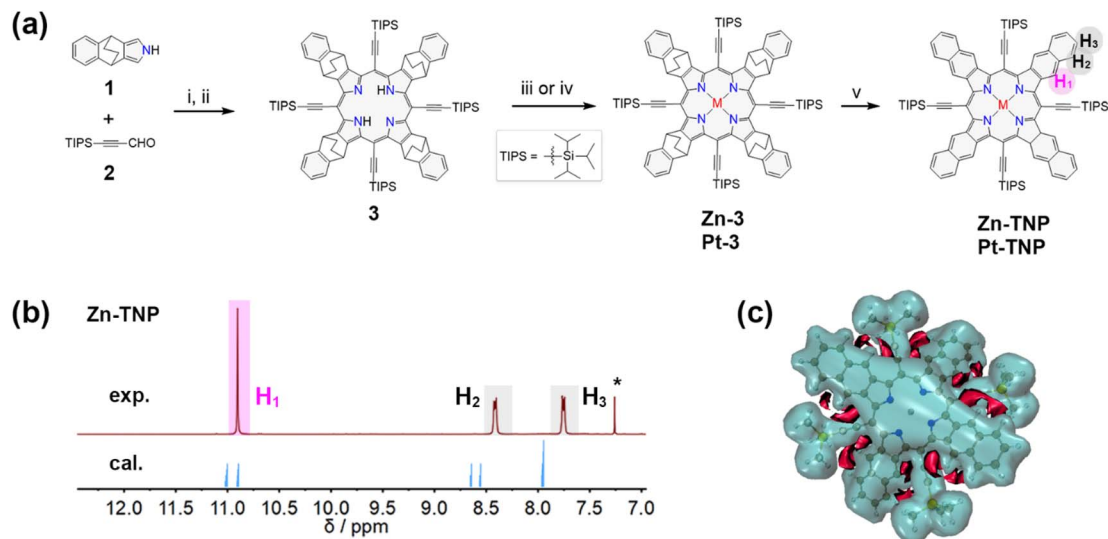


Fig. 2 (a) Synthesis of BCOD and π -extended porphyrins: (i) $\text{BF}_3 \cdot \text{OEt}_2$, CH_2Cl_2 , -78°C , 2 h; (ii) TCQC, r.t., 30 min; (iii) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, $\text{CHCl}_3/\text{MeOH}$, r.t., 3 h; (iv) PtCl_2 , NaOAc, AcOH, 118°C , N_2 , 24 h; (v) 300°C , 30 min, *in vacuo*. (b) ^1H NMR spectra of Zn-TNP: experimental data (above) measured in CDCl_3 and simulated data (below). (c) 3D ICSS map of Zn-TNP (isovalue = 1.5). The shielding areas are transparent blue and deshielding areas are solid red.

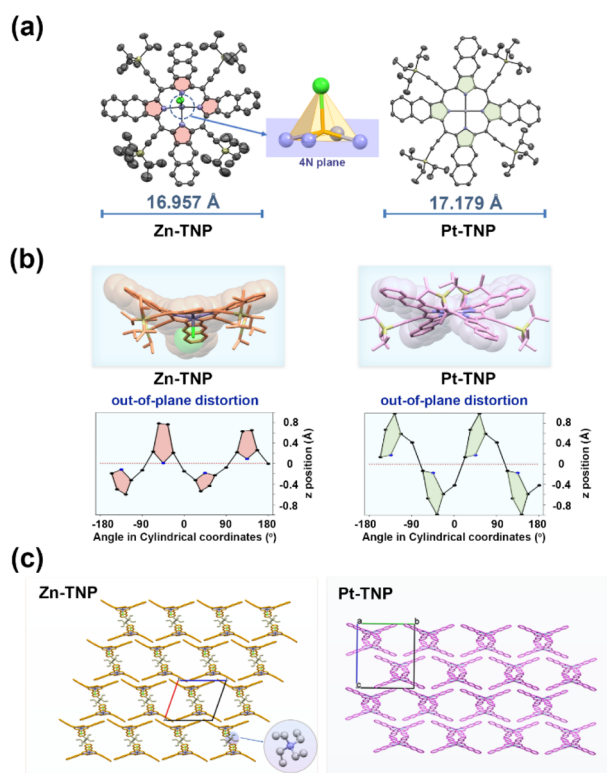


Fig. 3 (a) Top views of single crystal structures of Zn-TNP and Pt-TNP using an ORTEP diagram with thermal ellipsoids drawn at the 50% probability. (b) Side views and out-of-plane distortions of Zn-TNP and Pt-TNP. (c) Packing diagrams of Zn-TNP and Pt-TNP. In the packing views, *meso*-substituents are omitted for clarity.

significantly strengthen with more than 3-fold intensity and shift to the NIR region, peaking at 816 and 792 nm, respectively. The MCD spectrum of Zn-TNP shows derivative-shaped Faraday

A_1 terms with a pair of opposite signs at the absorption of B_{00} (549 nm) and Q_{00} (816 nm), respectively, indicating the presence of a highly symmetrical structure and degenerate excited states.⁴⁴ The Faraday A_1 terms of Zn-TNP show a negative-to-positive sign sequence in ascending energy, indicating that the energy difference between HOMO and HOMO-1 (ΔHOMO) is larger than that between LUMO and LUMO+1 (ΔLUMO).⁴⁵ The MCD pattern of Pt-TNP is identical to that of Zn-TNP. Compounds 3 and Zn-3 show fluorescence bands at 742 nm and 679 nm (Fig. S25 and S26[†]), respectively, while Zn-TNP shows a red-shifted fluorescence band at 847 nm (Fig. 4b, purple line). The Pt complexes exhibit room temperature phosphorescence (RTP). Pt-3 shows phosphorescence emission at 823 nm with a shoulder at 930 nm (Fig. S27[†]). For Pt-TNP, the RTP was detected in the range from 1000 to 1400 nm in deaerated toluene, showing the maximum at 1106 nm (Fig. 4b, red line). The phosphorescence band of Pt-TNP is located in the NIR-II region and more red-shifted than that of any other reported Pt-coordinated porphyrins.^{21,46} Moreover, Pt-TNP has a very large Stokes shift of 314 nm, making it a potential NIR-II phosphorescence probe for biomedical imaging. In air-saturated toluene, the RTP of Pt-TNP could also be observed with reduced intensity, and the singlet oxygen ($^1\text{O}_2$) generation capacity of Pt-TNP was revealed by the finding of a $^1\text{O}_2$ phosphorescence peak at 1270 nm (Fig. 4c, black line). The $^1\text{O}_2$ generation abilities of Pt-TNP and Zn-TNP were compared utilizing 1,3-diphenylisobenzofuran (DPBF) as a singlet oxygen scavenger (Fig. 4d, S34 and S35[†]). Under laser irradiation (808 nm , 10 mW cm^{-2}), the absorbance of DPBF in toluene exhibited no significant change without the addition of porphyrin compounds, but decreased significantly in 21 s with the presence of Pt-TNP. Furthermore, Pt-TNP exhibited excellent photostability, whereas Zn-TNP was unstable under



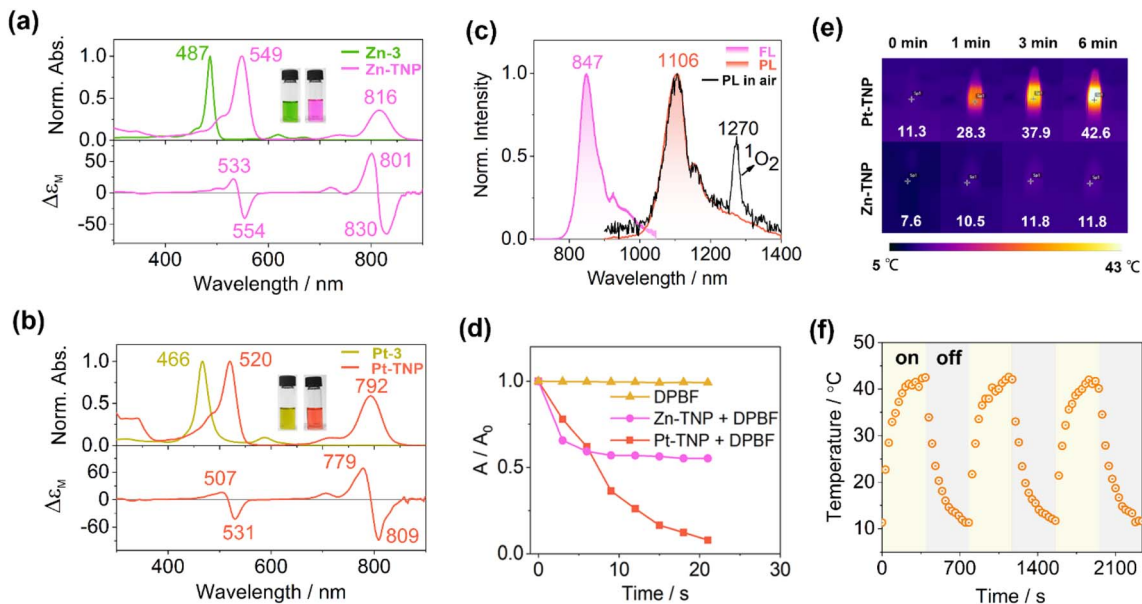


Fig. 4 (a and b) Absorption spectra of Zn-3, Zn-TNP, Pt-3 and Pt-TNP in toluene, and the MCD spectra of Zn-TNP and Pt-TNP in toluene. Inset: solution photographs of Zn-3, Zn-TNP, Pt-3, and Pt-TNP. (c) Fluorescence spectrum of Zn-TNP ($\lambda_{\text{ex}} = 549$ nm, purple line) in toluene, and phosphorescence spectra of Pt-TNP in deaerated and air-saturated toluene ($\lambda_{\text{ex}} = 520$ nm, red line and black line). (d) The absorption changes at 415 nm of DPBF, Zn-TNP + DPBF, and Pt-TNP + DPBF in toluene under 808 nm (10 mW cm^{-2}) laser irradiation within 21 s. (e) Thermal images of Pt-TNP and Zn-TNP ($30 \mu\text{mol}$) under 808 nm laser irradiation (0.35 W cm^{-2}). (f) Heating-cooling cycles for Pt-TNP ($30 \mu\text{mol}$) under 808 nm laser irradiation (0.35 W cm^{-2}).

irradiation and underwent rapid photobleaching (Fig. 4d and S36[†]). Previous research has demonstrated that zinc porphyrins can undergo photo-oxidation upon light exposure.^{47,48} The easier photodegradation of Zn-TNP may be attributed to its better oxygen affinity than Pt-TNP (Fig. S11, S18 and S19[†]), while the detailed mechanism still requires further investigation.^{49,50} The photothermal conversion performance of Pt-TNP and Zn-TNP was investigated in toluene under 808 nm (0.35 W cm^{-2}) laser irradiation. After 6 minutes of irradiation, the Pt-TNP solution had a temperature increase of over $30 \text{ }^\circ\text{C}$, whereas the Zn-TNP solution only increased by around $4 \text{ }^\circ\text{C}$ due to photostability (Fig. 4e and S33[†]). The heating-cooling measurements of Pt-TNP demonstrated excellent repeatability after three cycles (Fig. 4f and S30[†]). A time constant (τ) of 120.05 was obtained by linearly fitting time (t) as a function of the negative natural logarithm of the driving force temperature ($-\ln \theta$) at the cooling stage (Fig. S32[†]). The calculated photothermal conversion efficiency for the Pt-TNP solution was 78%.

DFT calculations were performed on a series of Pt porphyrins to evaluate the effects of *meso*- and β -substituents on their energy gaps (Fig. 5a and S39[†]). The *meso*-phenyl, β -non-fused ($N = 0$) platinum porphyrin Pt-TPP has degenerate LUMO/LUMO+1 and near-degenerate HOMO/HOMO-1, showing a large HOMO-LUMO gap of 3.05 eV. The naphthalene-fusion ($N = 2$) of Pt-TPP considerably lifts its a_{1u} -type HOMO-1 but has little effect on the a_{2u} -type HOMO, resulting in a HOMO/LUMO switch and a huge HOMO/HOMO-1 splitting with a largely reduced HOMO-LUMO gap of 2.24 eV in Pt-TPTNP (Fig. S48[†]). By replacing the phenyl group with either the electron-withdrawing pentafluorophenyl group or the electron-

donating 4-*N,N*-dimethylphenyl group, the naphthoporphyrin undergoes a simultaneous increase or decrease in both HOMO and LUMO energy levels, resulting in a very small change of the HOMO-LUMO gap. In contrast, the *meso*-alkynyl Pt-TNP (where triisopropylsilylethynyl is replaced by trimethylsilylethynyl) exhibits not only a significantly elevated HOMO consistent with its *meso*-phenyl counterpart, but also a substantially reduced LUMO due to the presence of electron-withdrawing alkynyl groups. The *meso*- β double regulation of Pt-TNP efficiently reduces the HOMO-LUMO gap to 1.92 eV, with the electron density extending to the fused naphthalenes on the HOMO and *meso*-alkynyl groups on the LUMO. It is noteworthy that the extended electron-density distributions towards alkynyl groups are exclusively observed in the LUMOs, but not in the HOMOs; therefore, conjugative extension could potentially play a substantial role in the large energy decreases of the LUMOs. Additional computational analysis reveals that replacing trimethylsilyl groups with H has a negligible impact on the HOMO/LUMO energy levels. By introducing electron-withdrawing groups like $-\text{CF}_3$ and $-\text{CN}$ into the alkynyl groups, the HOMO-LUMO gaps are further reduced to 1.80 eV and 1.66 eV, respectively (Fig. S40[†]). This energy-gap decrease is accompanied by a further extension of the electron density towards the terminal group.

The optimized structures of Pt-TNP and Zn-TNP are distorted, but they exhibit varying degrees and patterns of distortion compared to the single-crystal structures (Fig. S53[†]). These distortions may be caused by steric effects and further influenced by the crystal-packing forces. We successfully optimized Zn-TNP for both saddled (*sad*-Zn-TNP) and ruffled (*ruf*-Zn-TNP)



Based on the optimized structure of **Pt-TNP** and **Zn-TNP**, we evaluated the ring currents and induced magnetic shielding with a nucleus-independent chemical shift⁵² (NICS), anisotropy of the induced current density⁵³ (ACID), and the gauge-including magnetically induced current^{54,55} (GIMIC) calculations (Table S7 and Fig. S76–S78†). The NICS(0) values are negative in both the fused naphthene and porphyrin core for both compounds. The diatropic ring currents of **Zn-TNP** and **Pt-TNP** continuously flow throughout the whole structure, showing the global aromaticity of these two compounds. Additionally, localized diatropic ring currents are observed on the naphthalene moieties and the inner 16-bond porphyrin core.

Conclusions

In summary, we successfully synthesized porphyrin complexes with remarkable red-shifted NIR absorption and emission (ranging from 800 to 1200 nm) by tailoring the molecular energy levels through *meso*- and β -substituents. The electronic structures and optical properties of target *meso*-alkynyl naphthoporphyrin complexes **Zn-TNP** and **Pt-TNP** were fully elucidated *via* spectroscopic measurements and theoretical calculations. The solid structures of the complexes were analyzed using single-crystal X-ray diffraction, revealing saddling or mixed saddling–ruffling distortions. **Zn-TNP** and **Pt-TNP** displayed Q bands at 816 nm and 792 nm, respectively. **Zn-TNP** exhibited a fluorescence band at a wavelength of 847 nm. **Pt-TNP** exhibited room-temperature NIR-II phosphorescence at 1106 nm with a huge Stokes shift, and its ability to produce singlet oxygen was directly shown by the emission at 1270 nm. **Pt-TNP** also demonstrated excellent NIR photothermal conversion capacity. The dual functionality of **Pt-TNP** in singlet oxygen and heat generation makes it a promising candidate for combined photothermal/photodynamic therapy. While aromatic-ring-fusion is a well-established approach for reducing the HOMO–LUMO gap by HOMO-lifting, the additional functionalization of alkynyl groups in *meso* positions causes more than 100 nm of shifting in absorption/emission bands by LUMO-reduction when compared to their aryl-substituted counterparts. The DFT calculations provided an in-depth explanation of the correlation between the decrease in S_1/T_1 energy levels and the incorporation of *meso*- β substituents, as well as enhanced ISC activity in the Pt complex. The *meso*- β dual regulation of porphyrins effectively reduces the energy gap and modulates the excited states, offering a promising strategy for developing novel stable NIR materials.

Data availability

All experimental details including synthetic procedures, spectroscopic data, and theoretical calculation results, are available in the ESI.†

Author contributions

C. Q. carried out the synthesis, characterization, manuscript writing and theoretical calculations. X. G., Y. S., H. G. and F. C. contributed to the synthesis, characterization, and data analysis. C. Q., H. G. and Y. Z. performed the single-crystal X-ray diffraction measurements and analysis. F. W. and Z. S. designed and supervised the project, and revised the manuscript. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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