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Chemical Synthesis

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Atom-mutual-embedding strategy fuses four rings into rare tetrahexacyclic system

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Precise skeletal manipulation of polycyclic aromatic systems remains a formidable synthetic challenge, particularly in achieving controlled ring-opening and reorganization into unified conjugated frameworks. Although significant progress has been made in aromatic ring modification through ring contraction[1,2], expansion[3-15], and single-ring transformations[16-21] [Figure 1A], the precise fusion of multiple aromatic rings with simultaneous control over both connectivity and electronic properties at the atomic level remains a formidable challenge. Xia *et al.* now address this gap with a mutual-embedding strategy that fuses four 5-membered aromatic rings (two organic isoxazoles and two rhodapentalene-based metalla-aromatics) into a single metal-bridged 6/6/6/6-membered scaffold. Key to this breakthrough is the selective integration of nitrogen atoms into metal-carbon bonds and the formation of a stabilizing metal bridge between isoxazole units. The resulting π-conjugated system exhibits unprecedented thermal stability (up to 160 °C) and enhanced Near Infrared (NIR) properties, surpassing precursor performance [Figure 1B][22].

This study elucidates the intricate mechanism of rhodium-mediated polyannulation between benzisoxazoles and rhodapentalenes, which initiates through nucleophilic attack at the C7 position of the metallacycle to form **intermediate A**. Subsequent electron delocalization, N–O bond cleavage, and rhodium coordination generate imide species **C**, culminating in aryl migration and cyclization to afford product **3a** via a concerted "mutual embedding" process that simultaneously incorporates nitrogen into the Rh-C1 bond and carbon into the N–O linkage. For the construction of more complex 6/6/6/6/6-fused systems, mechanistic investigations reveal that $AgBF_4$-mediated ligand exchange produces pivotal **intermediate 6**, with subsequent $HBF_4{\cdot}Et_2O$ treatment inducing oxygen migration and nitrogen insertion through acid-promoted C–O/N–O bond cleavage of protonated species **E**. Control experiments demonstrate competing dimerization pathways under specific conditions, highlighting the delicate balance required for selective polycycle

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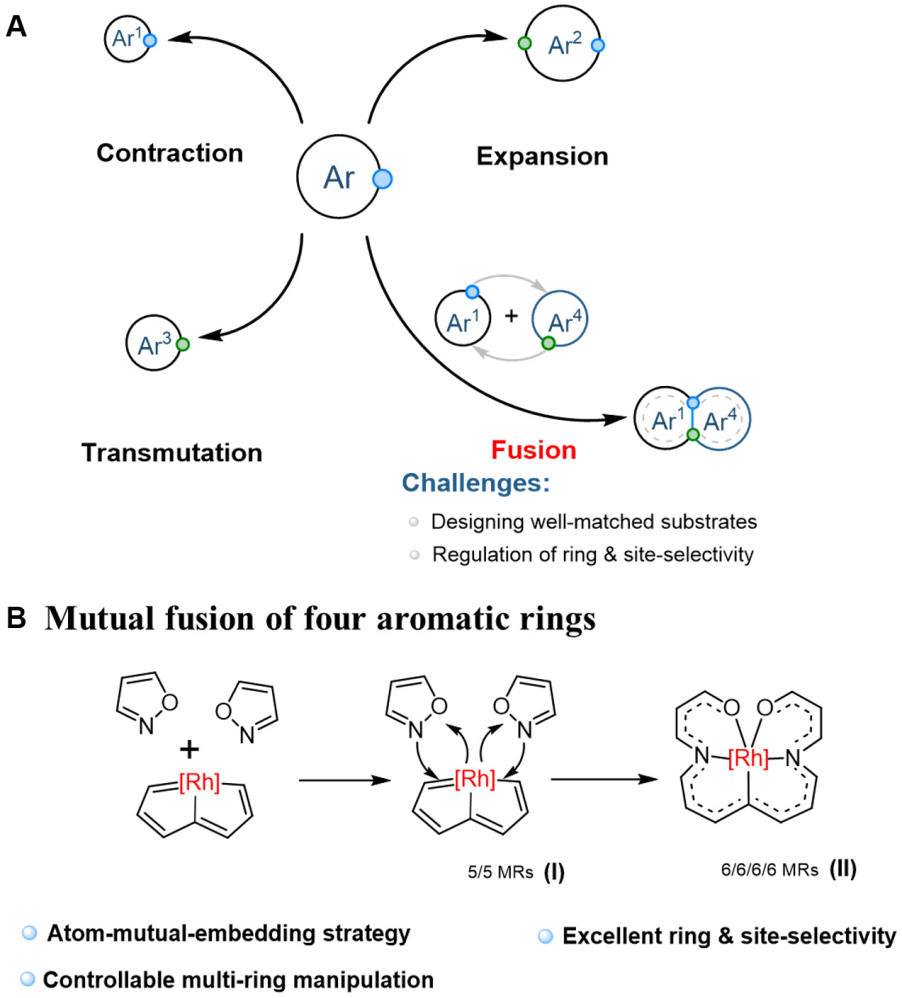

Figure 1. (A) Single-ring aromatic compound editing via main group atom manipulation (previously reported); (B) Mutual fusion of four aromatic rings (Figure 1A and B is reproduced with permission[22]. Copyright 2025, American Chemical Society).

formation [Figure 2A]. The transformation exhibits remarkable substrate generality, converting diverse 1,2-benzisoxazole derivatives into corresponding 6/6/6/6-fused products (**5a-5j**) in 50%-95% yields [Figure 2B].

While metallated pyridine frameworks are known, complex **5a** represents the first example incorporating two fused metallapyridine units, creating a unique naphthyridine derivative that expands conjugated polycyclic systems. Spectroscopic studies reveal **5a-5j** exhibit significant redshifted absorption [Figure 3A] compared to raw materials (**1**), with Time-Dependent Density Functional Theory calculations confirming narrowed Highest Occupied Molecular Orbital (HOMO)-Lowest Unoccupied Molecular Orbital (LUMO) gaps [Figure 3B]. These compounds exhibit NIR fluorescence, exceptional thermal stability [Figure 3C] and photostability [Figure 3D].

In summary, this work by Xia *et al.* reviews recent advances in the transformation strategies of aromatic compounds, with a particular focus on structural modifications achieved through single-atom skeleton editing and polycyclic fusion strategies. The introduction of aromatic compounds has opened up new possibilities for polycyclic skeleton editing, demonstrating the potential to enhance structural diversity and performance through the fusion of multiple metalloaromatic and organic aromatic systems. Future research

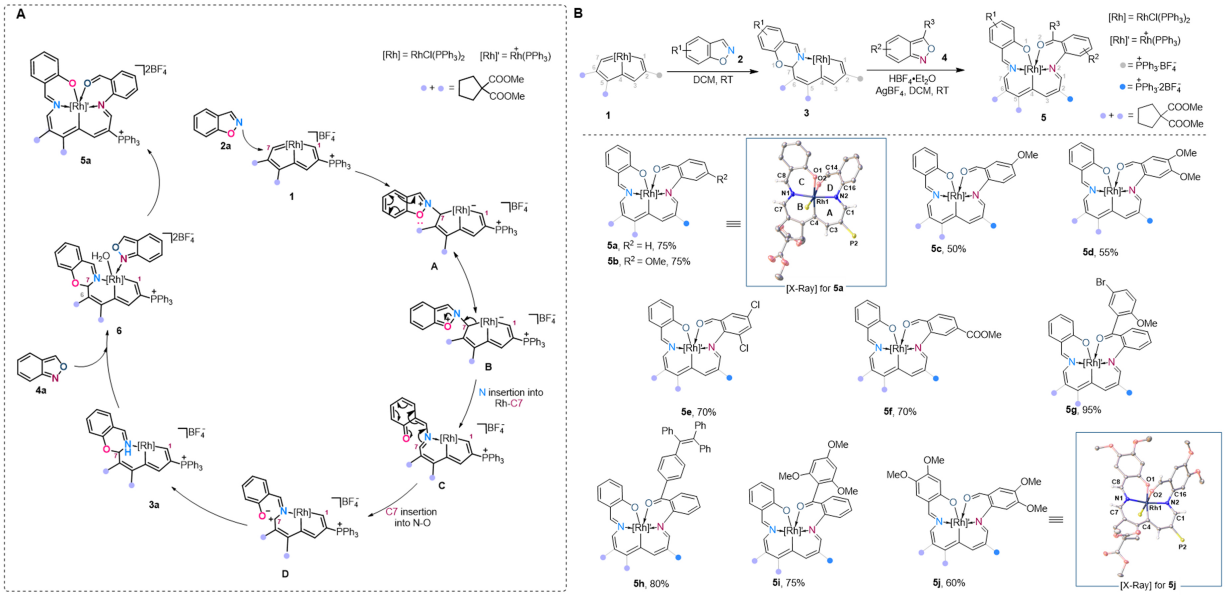

Figure 2. (A) Reaction mechanism and (B) Substrate scope. (Figure 2A and B is reproduced with permission[22]. Copyright 2025, American Chemical Society).

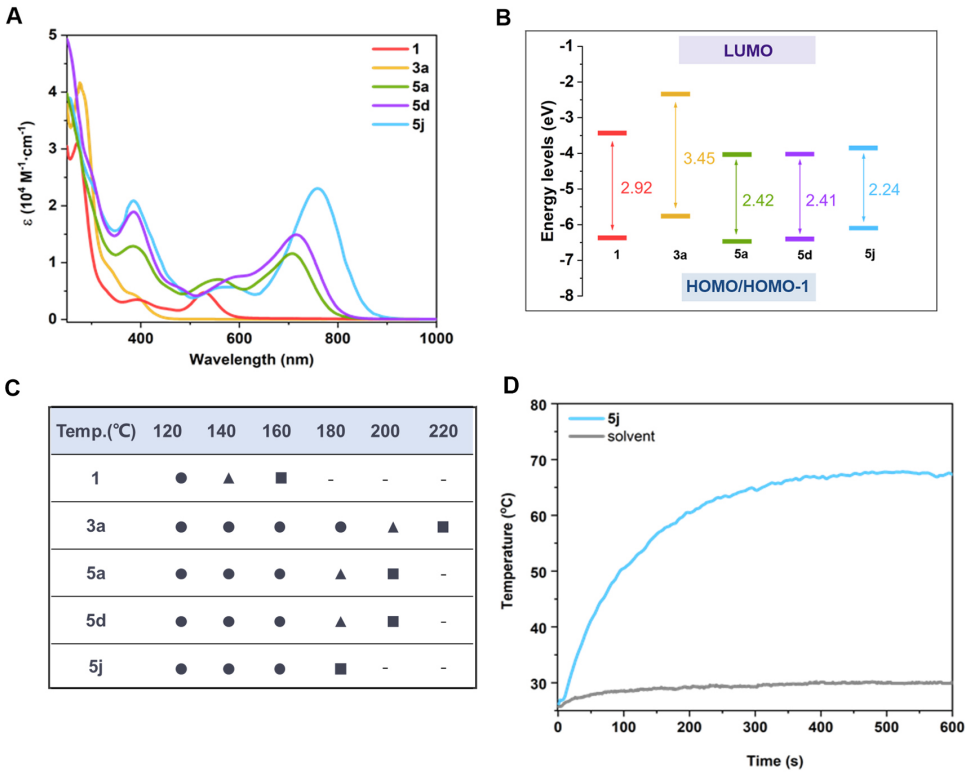

Figure 3. (A) UV–Vis-NIR absorption spectra of **1**, **3a**, **5a**, **5d** and **5j**; (B) Calculated HOMO and LUMO energy levels; (C) Thermal stability of complexes **1**, **3a**, **5a**, **5d** and **5j** in the solid-state after heating at different temperatures in air for 3 h. ● = stable, ▲ = partly decomposed, ■ = completely decomposed; (D) Photothermal conversion of **5j** (0.100 mg/mL in CH_3CN) under 808 nm (1.00 W/cm²) laser irradiation. HOMO: Highest Occupied Molecular Orbital; LUMO: Lowest Unoccupied Molecular Orbital. (Figure 3A-D is reproduced with permission[22]. Copyright 2025, American Chemical Society).

should further explore the applications of these strategies in optoelectronic and biomedical fields to enable more extensive functional molecular design.

DECLARATIONS

Authors' contributions

Writing and revision: Ren, Z.; Wei, L.; Ren, S.
Conceptualization and Project guidance: Pan, Y. M.; Tang, H. T.

Availability of data and materials

Not applicable.

AI and AI-assisted tools statement

Not applicable.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

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Consent for publication

Not applicable.

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