Not-So-Triyne Route to Heteroarylene and Arylene Macrocycles

**Significance:** This is the first reported synthesis of macrocyclic π-conjugated structures featuring both benzene and heterocycle units. Isolated yields up to ~85% and stereochemical purity up to ~95% ee are reported, though it is difficult to achieve both simultaneously. Bis- and tri-thiophene substrates produce trimers. While absorbance maxima were red-shifted with increasing thiophene rings, fluorescence maxima were not, indicating poor conjugation through the benzene ring vertices. However, this resulted in large Stokes shifts (90–120 nm) for these structures.

**Comment:** Ligand selection was found to be crucial for stereoselectivity, with QuinoxP* overall performing well. In trimer-forming systems, preference for dimer or trimer can also be tuned by ligand choice. The proposed mechanism is two rounds of metallacyclopentadiene formation followed by [2+2+2] cyclization. Stereochemistry is determined by the second [2+2+2] cyclization step. While thiophene-based systems performed well, attempts to use furans resulted in poor yields and stereoselectivity.

**Representative reaction:**

\[
\text{[Rh(cod)]BF}_4 \text{ (10 mol\%)} \\
(R,R)-\text{QuinoxP* (10 mol\%)} \\
\text{DCE, r.t. to 60 °C} \\
45\% \text{ yield} \\
52\% \text{ ee}
\]

**Selected compounds:**

- 38% yield 69% ee
- 47% yield >99% ee
- 50% yield