Significance: Mastalerz and co-workers report an unusual even-numbered bromination of triptycene tris(thiadiazoles), yielding regioselectively di-, tetrabromo-, and hexabromotriptycenes with two bromines each on the same phenyl ring. These brominated compounds will be useful in the synthesis of π-conjugated polymers of intrinsic microporosity and small electron acceptors.

Comment: Given that the C–C bond lengths of the phenyl rings are alternating, and hence the phenyl rings exhibit more olefinic than aromatic character from X-ray single crystal structure of 1, the mechanism for this unusual even-numbered bromination is proposed to involve 1,4-addition of Br₂, followed by subsequent re-aromatization of the phenyl ring by oxidation by Br₂ or FeBr₃. It is also proposed that this 1,4-addition–oxidation sequence is favored over electrophilic aromatic substitution. Furthermore, to demonstrate the utility of these monomers in the synthesis of conjugated polymers, dibromotriptycene 2 has been shown to undergo facile Suzuki–Miyaura cross-coupling.