**Significance:** A 5,5′-bicalixarene scaffold was incorporated into the linear backbone of a soluble conjugated polymer 5 via Glaser-type coupling. Monomer 4 synthesis relies on oxidative coupling of calixarene 1, followed by deprotection and selective triflation. Next, the triflate was replaced with TES-acetylene, because direct cross-coupling of 3 with 1,4-diethynylbenzene failed. Deprotection of the alkyne and installation of solubilizing groups furnished the desired monomer in 5% overall yield.

**Comment:** Access to a closed (capsule-type) conformation in bicalixarenes greatly enhances complexation properties of the calixarene scaffold. Indeed, polymer 5 fluorescence ($\lambda_{\text{abs}} = 420$ nm, $\lambda_{\text{em}} = 450$ nm, $\Phi_{FL} = 0.37$) is efficiently quenched by NO vapor. Importantly, a brief application of low vacuum to remove NO completely restores the fluorescence, indicating that the complexation is reversible.