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Facile synthesis of mixed O, S or Se bearing hexasubstituted benzenes and their potential as Cu(II) ion probe†

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The present study offers a facile route for the synthesis of unsymmetrical hexasubstituted benzenes bearing alternate heteroatoms (O, S and Se) with the formula [1,3,5-(RSeCH₂)₃-2,4,6-(R'ECH₂)₃C₆] (E = O, S or Se). The synthetic protocol involves the use of an *in situ* generated tris(selenonium) ion followed by treatment with another nucleophile affording the targeted species in >70% yields. The unsymmetrical hexasubstituted derivatives were characterized on the basis of physicochemical and spectroscopic data and in a representative case with single crystal X-ray study. The current work assumes great significance as the potential of these species as “turn-off” chemical sensors for Cu²⁺, which is a biologically and environmentally crucial metal ion, was also successfully demonstrated by **5a** which bears alternate oxygen and selenium centres.

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Introduction

In continuation to our studies on polyorganoselenium compounds,¹ we further focused our interest towards the synthesis of organoselenium species with heteroatomic donor combinations (O or S) under certain fundamental considerations as functional materials. Indeed, selenium in a polynucleating organic species with an alternately substituted heteroatom might reveal unique and discriminatory functional behaviors of species synergistically in a more precise and selective manner compared to their individual analogues. Factually, the presence of chalcogens in an organic species and their interactions at inter- and intramolecular levels have shown influence in stabilizing the structural motif besides controlling and regulating the molecular function.^{2–4} In many instances, due to the inherent peculiarities, organochalcogen derivatives supersede other main group elements in terms of their functional properties and are best exemplified for their potential as advanced materials with attractive electronic, biological, catalytic and recognition properties.^{5–8} Nevertheless, important prospects of organoselenium chemistry remain in the design and synthesis of new mixed chalcogen or heteroatom based

organic species for evaluating their diverse functional behaviors and unforeseen applications that are possibly not observable in their simpler analogues.

In this regard, studies on mixed chalcogen based hexasubstituted benzenes present an interesting avenue for newer functions due to their conformational behavior. For example, the oxygen substituted derivatives are well recognized for their inclusion phenomenon.^{9,10} Similarly, derivatization or synthesis of hexasubstituted benzenes bearing heteroelements (C, Se, Ge, Sn, N or P) finds considerable research interest with potentially new applications in inorganic, organometallic and analytical chemistry. Although fundamentally interesting, the synthesis of such species with mixed heteroatomic combinations of hexasubstituted benzenes and their applications remain unexplored. Therefore, a synthetic protocol for mixed chalcogen or chalcogen–heteroatom bearing hexa-substituted benzenes remains a challenging issue and studies on such systems are still awaited. Keeping these views in mind, we herein describe a synthetic protocol for the synthesis of mixed O, S or Se bearing hexasubstituted benzenes and further their potential in an identified system as highly selective chemical sensors for the biologically and environmentally crucial Cu²⁺ ion for analytical applications.

Results and discussion

Practically and as an overall synthetic strategy, 1,3,5-tris(bromomethyl)-2,4,6-tris(chloromethyl)benzene appeared to be a unique starting electrophilic precursor suitable for successive

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† Electronic supplementary information (ESI) available: Copies of ¹H, ¹³C, and ⁷⁷Se NMR and ES-MS spectrum of **2a**, **3a**, **4a**, and **5a**, fluorescence data, crystallographic data and refinement details for **2a** and **3a** along with corresponding crystal information files (CIF). CCDC 1894584 and 1894585. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/c9dt00465c