Supramolecular Assembly

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Functional Sulfur-Doped Buckybowls and Their Concave–Convex Supramolecular Assembly with Fullerenes

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***Abstract:** Buckybowls are fascinating components of supramolecular assemblies owing to their unique bowl-shaped π-surfaces. Herein we present a protocol for the functionalization of a sulfur-doped buckybowl, trithiasumanene, via a brominated intermediate, from which thiolated trithiasumanenes were derived. The curved surface and electron-donating properties of thiolated trithiasumanenes promote their ready assembly with fullerenes to form concave–convex complexes. The supramolecular assembly behavior in solution was investigated by NMR analysis. The structures of supramolecular complexes were unambiguously characterized by crystallography. The crystals of the concave–convex complexes showed high thermal stability and photoconductivity.*

Buckybowls, viewed structurally as a substructure of fullerenes[1] or the cap of carbon nanotubes,[2] have attracted much attention.[3] Their bowl-shaped conjugated structure leads to asymmetrical polarized concave–convex π-faces,[3,4] which are particularly attractive for supramolecular assembly.[5] The concave π-face of buckybowls has a higher electron density than the opposite convex π-face.[5a,6] Buckybowls tend to stack into a columnar supramolecular structure in a concave–convex fashion,[7] although packing devoid of a columnar structure was also observed.[8] Meanwhile, the electron-rich concave π-face of buckybowls can serve as an electronically and geometrically suitable electron-donating host for fullerenes.[6a,9] Doping of the buckybowls with heteroatoms,[10] such as sulfur and nitrogen, can enhance their electron-donating and polarizing ability,[10e,11] thus leading to stronger supramolecular interactions between buckybowls and electronic-deficient acceptors.[10e]

Besides heteroatom doping, functionalization with adaptable substituents is one of the most promising strategies to modulate and reinforce the supramolecular assembly of buckybowls. The substituents can not only tune the electronic nature of buckybowls,[5a,12] but can also introduce additional supramolecular interactions,[5b–d] such as hydrogen bonding. In general, multiply substituted buckybowls are needed to efficiently amplify the electronic effects and promote the supramolecular assembly.[5a–d,12,13] For example, by employing a pentathiolated corannulene, Scott and co-workers realized the first supramolecular assembly of buckybowls with C_{60} in solution.[5a] As another example, Aida and co-workers constructed electric-field-responsive liquid crystals[5b] and chiral supramolecular polymers[5c] by using deca- or pentathiolated corannulenes bearing multiple hydrogen-bonding sites on the peripheral thiol groups. The combination of heteroatom doping and multisubstitution can lead to more effective building blocks for the construction of supramolecular architectures. However, studies on the functionalization and application of heteroatom-doped buckybowls in supramolecular assembly have been rare.

Herein we report a protocol for the functionalization of a sulfur-doped buckybowl, trithiasumanene (**1**), by perbromination and nucleophilic substitution. The hexathiolated trithiasumanenes **3**–**5** were readily synthesized by this strategy. The curved and electron-rich nature of hexathiolated trithiasumanenes makes them good hosts for supramolecular assembly with fullerenes. The supramolecular assembly in solution was confirmed and characterized by NMR spectroscopy and fluorescence quenching. The crystal structures of the complexes clearly revealed close concave–convex π–π interactions between the hexathiolated trithiasumanenes and fullerenes, as well as the packing structure of the supramolecular complexes in the crystalline state. The crystal of the $\mathbf{3}\supset C_{60}$ complex showed remarkably high thermal stability and intrinsic charge-carrier transporting that was not achieved by the drop-cast $\mathbf{3}/C_{60}$ 1:1 mixture.

Halogenated buckybowls are key intermediates for the synthesis of functionalized, especially multisubstituted, buckybowls.[14] Trithiasumanene (**1**) was perbrominated with bromine in the presence of a catalytic amount of iron powder at 80 °C to afford perbromotrithiasumanene (**2**) in 95 % yield (Figure 1 a; see also Figure S1 in the Supporting Information). Compound **2** is the first reported perbrominated buckybowl, and its chemical identity was characterized by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (see Figure S2). Only one dominant peak in the mass spectrum was observed, with an isotopic distribution pattern identical to that calculated for compound **2** (see Figure S2). However, the poor solubility of **2** in common organic solvents hindered its further structural elucidation.

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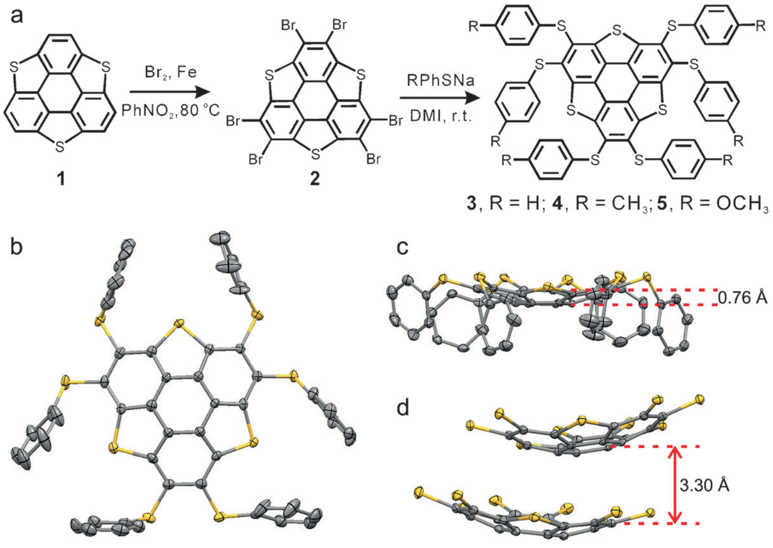

Figure 1. a) Synthetic route towards hexathiolated trithiasumanenes **3**–**5** (DMI = 1,3-dimethyl-2-imidazolidinone). b) Top view and c) side view of **3**. d) Concave–convex dimer of **3** (phenyl groups are not shown). In (b–d), all hydrogen atoms have been omitted for clarity, and thermal ellipsoids are set at the 50% probability level.

The introduction of thiol groups at the periphery would enhance the electron-donating ability of trithiasumanene and thus promote its donor–acceptor supramolecular assembly with fullerenes.[5a, 12a] Hence, we carried out the thiolation of **2** with different aryl thiolates to produce hexakis(phenylthio)-trithiasumanene (**3**), hexakis(*p*-tolylthio)trithiasumanene (**4**), and hexakis(4-methoxyphenylthio)trithiasumanene (**5**) in 35–40% yield (see the Supporting Information). The mass spectra of **3**–**5** displayed one dominant peak, which matched the formulae of **3**–**5** perfectly (see Figure S3). Unlike **2**, **3**–**5** showed sufficient solubility in organic solvents, such as dichloromethane, toluene, and chloroform, to allow for their characterization by ^{1}H and ^{13}C NMR spectroscopy (see Figures S3–S6), which confirmed their proposed chemical structures as well as their high purity.

The detailed structure of the hexathiolated trithiasumanene **3** was determined by crystallography (see the Supporting Information).[15] Single crystals of **3** were obtained by slowly diffusing *n*-hexane into a solution of **3** in chloroform. The trithiasumanene core was decorated with six phenylthio groups (Figure 1a). The hub six-membered ring of the bowl in **3** showed slight bond alternation (1.393(8)–1.414(8) Å), whereas the outside rim of the flanking six-membered rings showed clearly elongated bond lengths (1.434(7) Å; see Figure S7). Compound **3** exhibited a shallower bowl depth (0.76 Å) and smaller Haddon π-orbital axis vector angle (6.2°) as compared to sumanene (1.11 Å and 8.8°;[16] Figure 1b), thus indicating less strain in trithiasumanene owing to the larger atomic radius of the doping sulfur atoms. In the crystal, **3** forms a concave–convex dimer by π–π interactions with a shortest bowl-to-bowl distance of 3.30 Å (Figure 1c), which is significantly shorter than that of pristine trithiasumanene (3.48 Å),[10a] hexabutoxytriselenasumanene (3.56 Å),[10b] and sumanene (3.86 Å),[16] thus implying the existence of strong π–π interactions between the bowls.

The optical properties of **3**–**5** were elucidated by UV/Vis and fluorescence spectroscopy. Compounds **3**–**5** have nearly identical absorption profiles (Figure 2a), with the highest absorption peak at 365 nm (log ε = 4.64) and a shoulder peak at 385 nm (log ε = 4.35), which can be assigned as the β and p absorption bands. The weak absorption peak (log ε = 3.38) located at 445 nm was assigned as the α absorption band, which corresponds to a HOMO–LUMO gap of 2.30 eV. Similarly, the fluorescence spectra of **3**–**5** were nearly identical, with emission at 464 nm (Figure 2a). The optical absorption and fluorescence of **3**–**5** are redshifted by 0.047 and 0.064 eV as compared to pristine trithiasumanene and by 0.052 and 0.088 eV as compared to hexabutoxyltrithiasumanene.[10a,b] These data revealed the strong perturbation effect of peripheral thiol groups on the electronic nature of trithiasumanene. The sulfur doping in the skeleton and peripheral thiol substituents was expected to greatly enhance the electron-donating ability of the buckybowl. From electrochemical measurements, compounds **3**–**5** showed a much lower

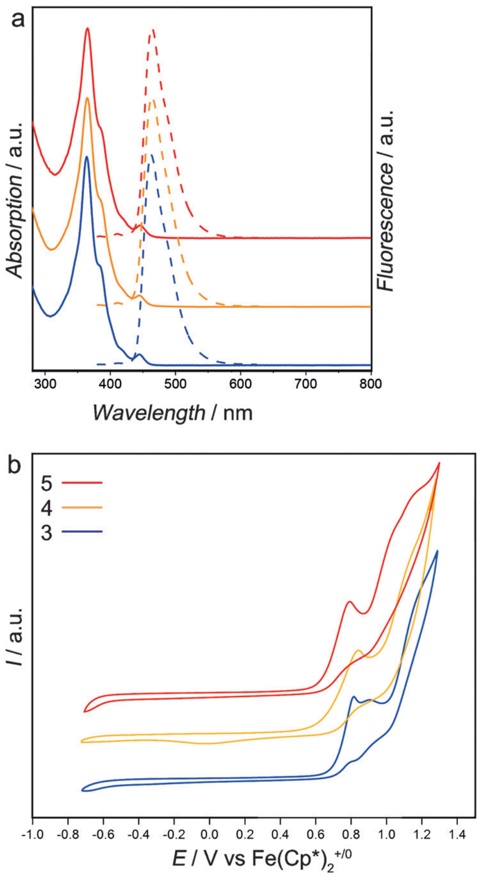

Figure 2. Optical and electrochemical properties of **3**–**5**. a) Absorption (solid lines) and fluorescence spectra (dashed lines) of **3**–**5** in CH_2Cl_2. b) Cyclic voltammograms of **3**–**5** in anhydrous CH_2Cl_2 containing 0.1 mol mL^{-1} tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte at a scan rate of 100 mV s^{-1}.

oxidation potential (0.74 V for **3**, 0.72 V for **4**, and 0.69 V for **5** versus FeCp$_2^{+/0}$; Figure 2b) in comparison with that of corannulene (1.57 V).[12b]

The curved π-surface in combination with their electron-rich nature renders **3**–**5** suitable supramolecular hosts for electron-deficient fullerene. The supramolecular assembly of **3**–**5** with fullerenes in solution was confirmed by NMR spectroscopy. Upon the addition of an equimolar amount of C$_{60}$ to solutions of **3**–**5**, the proton signals of the peripheral thiol group of **3**–**5** were shifted downfield by 0.037–0.030 ppm and 0.015–0.011 ppm (Figure 3) as a result of the deshielding effect of C$_{60}$, thus manifesting the formation of supramolecular complexes. Furthermore, hydrogen atoms H$_c$ closer to the buckybowl exhibited a downfield shift that was twice as large as that of the *meta* and *para* hydrogen atoms H$_b$ and H$_a$ (Figure 3), thus suggesting that C$_{60}$ locates at the concave center of trithiasumanene in the supramolecular complexes (see below). In contrast, the addition of C$_{60}$ to a solution of pristine trithiasumanene did not result in any shifting of the ^{1}H signal of the bowl, thus implying that multithiolation is critical for the formation of a supramolecular complex in solution.

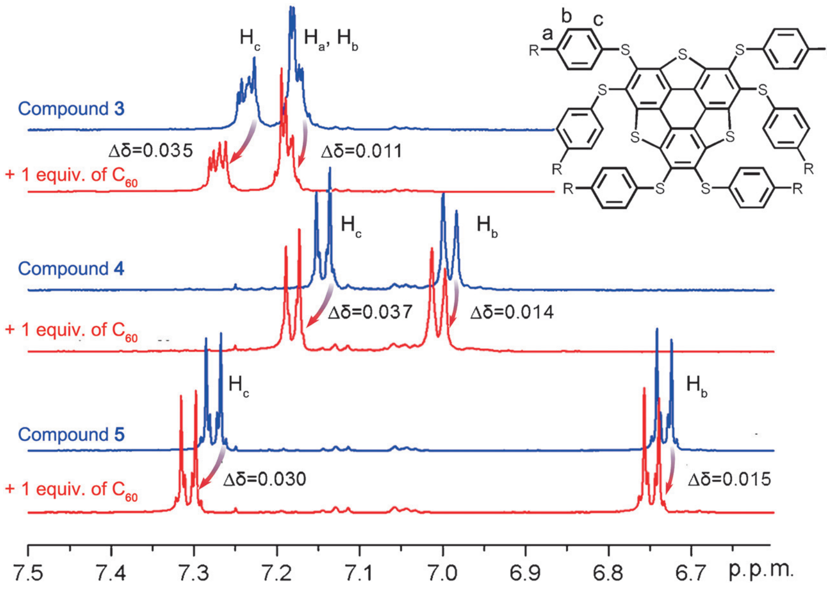

Figure 3. ^{1}H NMR spectra before (blue) and after (red) the addition of C$_{60}$ (1 equiv) to a solution of **3**–**5** (1.9×10^{-3} M^{-1}) in CS$_2$/CCl$_2$D$_2$ (3:1).

To understand the assembly behavior between **3**–**5** and C$_{60}$ further, we carried out NMR titrations and determined the binding constants of the supramolecular complexes ($K_a = (193\pm26)$ M^{-1} for **3**$\supset$C$_{60}$, (247 ± 32) M^{-1} for **4**$\supset$C$_{60}$, (395 ± 32) M^{-1} for **5**$\supset$C$_{60}$; see Figures S8–S13 and details in the Supporting Information). The binding constants of the complexes between **3**–**5** and C$_{60}$ are comparable with that of pentathiolated corannulene/C$_{60}$ complexes.[12a] Job plot analysis revealed the formation of 1:1 complexes between **3**–**5** and C$_{60}$ in solution, which was exemplified by the crystal structure of complex **3**$\supset$C$_{60}$. The formation of supramolecular complexes in solution was also supported by fluorescence quenching when C$_{60}$ was titrated into solutions of **3**–**5** (see Figure S14); this behavior indicates intermolecular charge–transfer interactions between **3**–**5** and C$_{60}$.

The detailed structure of the concave–convex complexes was validated by single-crystal X-ray diffraction (Supporting Information).[15] Upon the addition of *n*-hexane to a solution of **3** and C$_{60}$ (1:1) in carbon disulfide, single crystals of **3**$\supset$C$_{60}$ grew spontaneously within 2 days. In **3**$\supset$C$_{60}$, C$_{60}$ is located in the center of the bowl without any disorder in a concave–convex relationship with **3**. Notably, all the peripheral aryl thiol groups of **3** in the supramolecular complex point away from C$_{60}$ (Figure 4a). As a result, there is no direct interaction between the phenyl groups and C$_{60}$ (see Figure S15), and the concave–convex π–π interactions between the bowl and C$_{60}$ are dominant (Figure 4a; see also Figure S16). In contrast, the substituent groups wrapped around C$_{60}$ in the previously reported

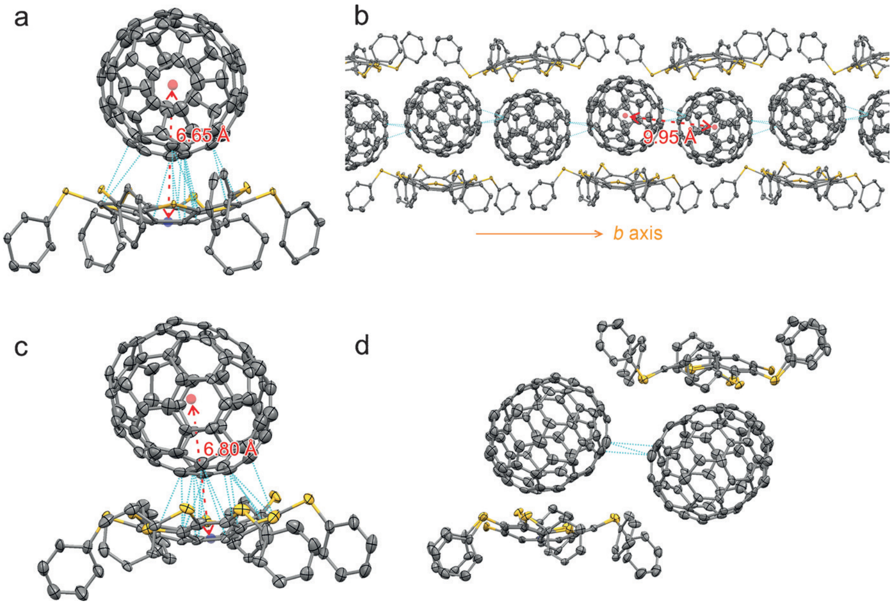

Figure 4. Concave–convex supramolecular complexes of **3** and fullerenes. a) Concave–convex complex **3**$\supset$C$_{60}$; b) one-dimensional supramolecular chain of **3**$\supset$C$_{60}$ along the *b* axis; c) concave–convex complex **3**$\supset$C$_{70}$; d) dimer of **3**$\supset$C$_{70}$. The centroids of fullerenes and the hub six-membered ring of **3** are represented as red and blue dots, respectively. The π–π interactions are represented by cyan dotted lines. All hydrogen atoms have been omitted for clarity, and thermal ellipsoids are set at the 30% probability level.

complexes of thiolated corannulenes and C_{60}.[5a,17] The UV/Vis/NIR spectrum of $\mathbf{3}{\supset}C_{60}$ crystals showed a charge-transfer band at 930 nm, which can be attributed to donor–acceptor charge transfer from the bowl of **3** to C_{60} (see Figure S17). However, we could not find the charge-transfer band in solution when C_{60} was titrated into the solution of **3** (see Figure S18). The shortest distance from the concave surface of **3** to C_{60} is 3.22 Å, and the distance from the centroid of hub six-membered ring of **3** to the centroid of C_{60} is 6.65 Å (Figure 4). These distances are shorter than those observed in an azabuckybowl/C_{60} complex (3.29 and 6.82 Å, respectively).[10e] The complex $\mathbf{3}{\supset}C_{60}$ can serve as a supramolecular building block and pack into a one-dimensional chain through π–π interactions between C_{60} cages (Figure 4b). In the one-dimensional supramolecular chain, the shortest distance between the surfaces and the centroids of the cages is 3.18 and 9.95 Å, respectively.

C_{70} can also assemble with **3**, as demonstrated by obtaining single crystals of $\mathbf{3}{\supset}C_{70}$ (see the Supporting Information).[15] As shown in Figure 4c, C_{70} sits in the concave surface of **3** to form a concave–convex complex. The shortest distance from the concave surface of **3** to the convex surface of C_{70} is 3.15 Å, and the intercentroid distance is 6.80 Å, thus demonstrating strong π–π interactions between the two structures (Figure 4c). The peripheral thiol groups adopted a conformation similar to that in $\mathbf{3}{\supset}C_{60}$. In contrast to $\mathbf{3}{\supset}C_{60}$, which packs into a one-dimensional chain, $\mathbf{3}{\supset}C_{70}$ only forms a dimer through π–π interactions (3.13 Å) between C_{70} cages (Figure 4c). Surprisingly, although the bowl framework was thought to be rigid, the bowl core of **3** was slightly deeper in both complexes as compared with that of its free form, as evidenced by X-ray crystallography (depth of 0.76 Å for **3** versus 0.83 Å for $\mathbf{3}{\supset}C_{60}$ and $\mathbf{3}{\supset}C_{70}$) and the Haddon π-orbital axis vector angle (6.2° for **3** versus and 6.6° for $\mathbf{3}{\supset}C_{60}$ and $\mathbf{3}{\supset}C_{70}$), probably to maximize the host–guest interactions.

In contrast to the ready efflorescence of $\mathbf{3}{\supset}C_{70}$ crystals, the single crystals of $\mathbf{3}{\supset}C_{60}$ were highly stable and maintained their crystallinity even after heating at 120 °C under vacuum for 12 h, as demonstrated by resolving the structure of an annealed crystal of $\mathbf{3}{\supset}C_{60}$.[15] The resolved structure showed that C_{60} was still assembled with **3** in a concave–convex manner, but that the cocrystallized solvent was partially lost after heating (see Figure S19). Interestingly, the orientation of C_{60} in $\mathbf{3}{\supset}C_{60}$ was changed, whereas the conformation of **3** remained intact after vacuum annealing (see Figure S19). The high stability of $\mathbf{3}{\supset}C_{60}$ crystals motivated us to investigate their photoconductivity by flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements.[7c,18] When photoexcited with 355 nm laser pulses, a single crystal of $\mathbf{3}{\supset}C_{60}$ mounted on a quartz rod showed isotropic transient conductivity with prompt-rise and slow-decay features (Figure 5; see also the Supporting Information). Its maximum transient conductivity $(\varphi\Sigma\mu)_{\max}$ was $2.9\times10^{-5}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ (Figure 5), which is lower than the conductivity of an azabuckybowl/C_{60} complex ($2.4\times10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$).[10e] However, a reference solid, composed of a drop-cast mixture of **3** and C_{60} in a 1:1 molar ratio, indicated a smaller conductivity transient: The maximum transient conductivity $(\varphi\Sigma\mu)_{\max}$ of drop-cast mixture was $0.7\times10^{-5}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ and thus about one-quarter of that observed for the single crystal of $\mathbf{3}{\supset}C_{60}$ (Figure 5). This result indicates that the formation of a supramolecular complex can enhance charge transfer, which could be useful in organic field-effect transistors.

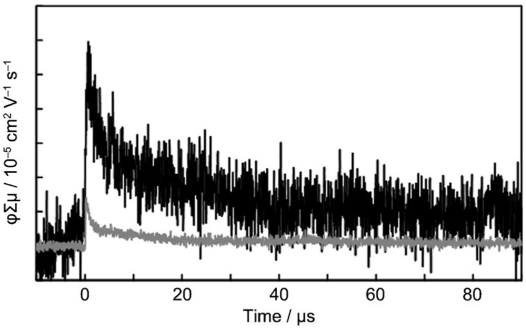

Figure 5. Typical conductivity transients observed for a single crystal of $\mathbf{3}{\supset}C_{60}$ (black) and a drop-cast solid composed of a mixture of **3** and C_{60} (gray). Photoexcitation was carried out by using 355 nm laser pulses with a photon density of 1.4×10^{16} photons cm^{-2} pulse^{-1}.

In summary, a synthetic protocol for the functionalization of trithiasumanene was developed that enabled the straightforward synthesis of versatile functional trithiasumanenes. The curved and electron-rich nature of hexathiolated trithiasumanenes makes them suitable electron-donating hosts for fullerene, with the formation of concave–convex supramolecular complexes. The supramolecular assembly in solution was confirmed and investigated by NMR spectroscopy and fluorescence quenching. The structures of the supramolecular complexes were validated unambiguously by crystallography, which revealed close π–π interactions between trithiasumanenes and fullerenes. The single crystals of $\mathbf{3}{\supset}C_{60}$ showed remarkable thermal stability and high photoconductivity. Our synthetic strategy in combination with supramolecular assembly enables the rational design of functional trithiasumanene structures and the construction of supramolecular architectures based on functional trithiasumanene. We expect our results to stimulate the investigation of heteroatom-doped buckybowls in supramolecular materials, organic nanostructures, and organic electronics.

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[15] CCDC 1480836, 1480837, 1480838, and 1480839 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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