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Communication

Designing a Solution-Stable Distannene: The Decisive Role of London Dispersion Effects in the Structure and Properties of $\{Sn(C_6H_2\text{-}2,4,6\text{-}Cy_3)_2\}_2$ (Cy = Cyclohexyl)

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ABSTRACT: The reaction of 1 equiv of the dimeric lithium salt of a new London dispersion effect donor ligand $\{Li(C_6H_2\text{-}2,4,6\text{-}Cy_3)\cdot OEt_2\}_2$ (Cy = cyclohexyl) with $SnCl_2$ afforded the distannene $\{Sn(C_6H_2\text{-}2,4,6\text{-}Cy_3)_2\}_2$ (**1**). The distannene remains dimeric in solution, as indicated by its room-temperature ^{119}Sn NMR signal (δ = 361.3 ppm) and its electronic spectrum, which is invariant over the temperature range of −10 to 100 °C. The formation of the distannene, which has a short Sn−Sn distance of 2.7005(7) Å and greatly enhanced stability in solution compared to that of other distannenes, is due to increased interligand London dispersion (LD) attraction arising from multiple close approaches of ligand C−H moieties across the Sn−Sn bond. DFT-D4 calculations revealed a dispersion stabilization of dimer **1** of 38 kcal mol^{-1} and a dimerization free energy of $\Delta G_{\text{dimer}} = -6$ kcal mol^{-1}. In contrast, the reaction of 2 equiv of the similarly shaped but less bulky, less hydrogen-rich $Li(C_6H_2\text{-}2,4,6\text{-}Ph_3)\cdot(OEt_2)_2$ with $SnCl_2$ yielded the monomeric stannylene $Sn(C_6H_2\text{-}2,4,6\text{-}Ph_3)_2$ (**2**), which is unstable in solution at ambient temperature.

Seminal work by Lappert and co-workers in the 1970s described the synthesis of the first σ-bonded stannylenes $Sn\{CH(SiMe_3)_2\}_2$[1,2] and $Sn\{N(SiMe_3)_2\}_2$[3,4] (the latter species was also reported by Zuckerman and co-workers).[5,6] X-ray crystallography subsequently established that whereas $Sn\{N(SiMe_3)_2\}_2$ is monomeric, $Sn\{CH(SiMe_3)_2\}_2$ exists in the solid state as the Sn−Sn bonded dimer $[Sn\{CH(SiMe_3)_2\}_2]_2$ with pyramidal tin coordination.[2] Since then, much effort has been devoted to understanding these heavier carbene analogues (ER_2, where E is a group 14 element) and the multiple E−E bonding in their R_2EER_2 dimers.[7−9] The folded, trans-pyramidalized configuration of the tin atoms in $[Sn\{CH(SiMe_3)_2\}_2]_2$ and in most other distannenes led to the description of the Sn−Sn bond as a nonclassical double bond.[10] This interaction is quite weak, and distannenes R_2SnSnR_2 typically dissociate into stannylene ($:SnR_2$) monomers in the solution and gas phases.[11] Variations in the tin−tin bonding also exist. For example, Weidenbruch's $\{Sn(C_6H\text{-}2\text{-}^tBu\text{-}4,5,6\text{-}Me_3)_2\}_2$ features pyramidalized geometry at only one of its tin atoms, with nearly planar geometry at the other.[12] This results in a weaker Sn−Sn interaction and an exceptionally long Sn−Sn separation of 2.910(1) Å. In contrast, Sekiguchi's distannene $\{Sn(SiMe^tBu_2)_2\}_2$ displays essentially planar geometry at both tin atoms and has an unusually high torsion angle of ca. 45° between the SnR_2 planes.[13] Sekiguchi and Apeloig showed that this complex remains dimerized in solution at ambient temperature (the only known acyclic distannene to do so) and possesses the shortest known Sn−Sn bond length (2.6679(8) Å) among acyclic distannenes.[14]

Much of the discussion of the bonding in distannenes has concerned the direct orbital interactions between the tin atoms.[9] However, in a collaborative study by Nagase and this laboratory, a computational examination of the bonding in these heavier main group analogues revealed that the London dispersion (LD) interaction is mainly responsible for the stability of their dimeric structures in the solid state.[15] More generally, the effects of LD interactions on the stability of organic molecules and NHC-coordinated main group compounds have been described by Schreiner and co-workers.[16,17] The origin of this stability in distannenes involves multiple close interligand contacts between C−H moieties across the Sn−Sn bond. This finding was later confirmed by Růžička and Hobza, who concluded that our initial calculations may have underestimated the importance of LD attraction in stabilizing heavier group 14 R_2EER_2 molecules.[18] The effects of noncovalent interactions in organometallic molecules have also been addressed.[19,20] We have since reviewed LD effects in organometallic complexes and concluded that several counter-intuitive phenomena are in fact hallmarks of intramolecular LD attraction.[21] Perhaps the most striking outcome of LD attraction is the often inverse relationship between steric congestion and structural features or reactivity. For example, we have previously shown that, because of LD attraction, increasing the steric demand of the ligands in ER_2 complexes results in the closure of the R−E−R angle, although the angle is normally expected to widen as the size of the R groups increases.[22,23] In a classic demonstration, Schreiner showed that a substituted hexaphenyl ethane derivative, hexa(3,5-di-

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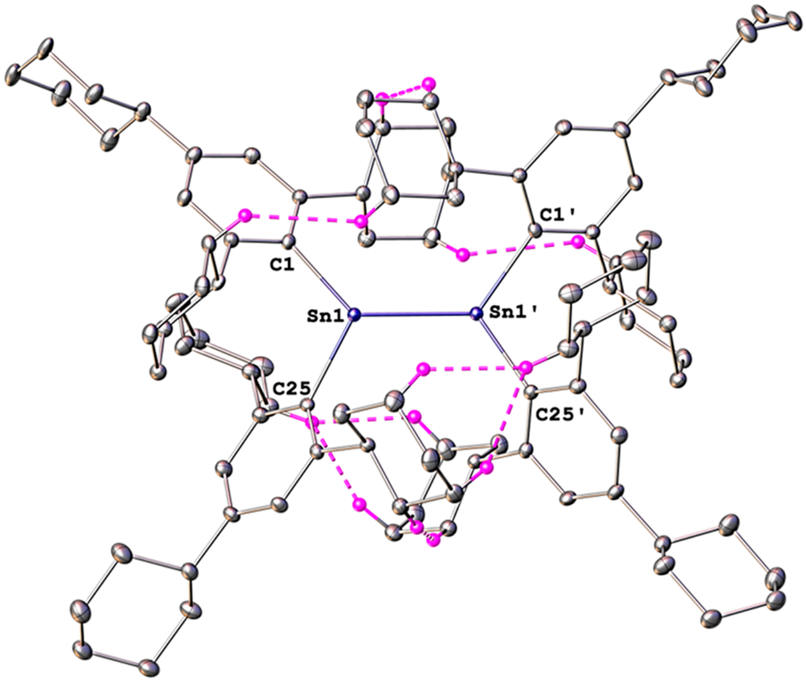

Figure 1. Molecular structure of $\{Sn(C_6H_2\text{-}2,4,6\text{-}Cy_3)_2\}_2$ (**1**) with thermal ellipsoids drawn at 30% probability. Interligand H−H contacts across the Sn−Sn bond below the sum of their van der Waals radii (ca. 2.4 Å) are indicated with dashed lines. All other hydrogens are not shown. Selected bond distances (angstroms) and angles (deg): Sn1−Sn1′ = 2.7011(7), Sn1−C1 = 2.182(3), Sn1−C25 = 2.189(3), and C1−Sn1−C25 = 106.80(11).

tert-butylphenyl)ethane, is stabilized by interactions between bulky substituents on the phenyl groups and more recently showed that the heavier hexaphenylditetrelanes are also stabilized by dispersion.[24,25] We therefore sought ligands that would produce stabilizing LD effects in distannenes.

Herein we demonstrate the dramatic effects of the LD stabilization arising from interligand H−C−H−C interactions of hydrocarbon substituents. Thus, the reaction of the new aryllithium reagent $\{Li(C_6H_2\text{-}2,4,6\text{-}Cy_3)\cdot(OEt_2)\}_2$ (Cy = cyclohexyl) with $SnCl_2$ affords the Sn−Sn-bonded distannene $\{Sn(C_6H_2\text{-}2,4,6\text{-}Cy_3)_2\}_2$ (**1**), which remains dimeric in solution even at elevated temperature. In contrast, the reaction of the less bulky $Li(C_6H_2\text{-}2,4,6\text{-}Ph_3)\cdot(OEt_2)_2$ with $SnCl_2$ yields the monomeric stannylene, $Sn(C_6H_2\text{-}2,4,6\text{-}Ph_3)_2$ (**2**). The LD attraction produced by the H−H contacts in the former species is decisive in the stabilization of the distannene. The increased thermodynamic stability conferred by LD attraction is further underlined by the inherent instability of the less sterically encumbered $Sn(C_6H_2\text{-}2,4,6\text{-}Ph_3)_2$ (**2**), which decomposes into intractable products in solution.

Owing to their ease of modification, aryl ligands feature prominently among structurally characterized organometallic complexes. This also is true for tin(II) complexes of the form $(SnR_2)_n$.[26] However, only one structurally characterized metal complex of any kind is known for the 2,4,6-tricyclohexylphenyl ligand. This was formed by the photolysis of $Ni(Br)_2(bipy)$ (bipy = 2,2′-bipyridine) in the presence of 2,4,6-tricyclohexylbromobenzene[27] rather than by salt metathesis. Almost simultaneously with that report, Fürstner and co-workers showed that the exceptional iron(IV) tetraalkyl complex $FeCy_4$ is stabilized by attractive interligand LD interactions between the cyclohexyl substituents, despite the presence of multiple accessible *β*-hydrogens which would typically react further to result in its decomposition.[28] Given these results and that distannenes have been shown to be stabilized by dispersion effects in the solid state, we suspected that the 2,4,6-tricyclohexylphenyl ligand might be capable of stabilizing a distannene in solution as well. When preparing 2,4,6-tricyclohexylphenyllithium (SI), we were encouraged by the fact that its diethyl ether complex has a dimeric structure with multiple close interligand H−H contacts in its crystal structure. In contrast, the less bulky 2,4,6-triphenylphenyllithium, which differs mainly in hydrogen content from the 2,4,6-tricyclohexylphenyl derivative, has a monomeric structure in which the lithium atom coordinates two diethyl ether molecules in the solid state.[29] Motivated further by this apparent anomaly, we investigated the different properties conferred by these two ligands on divalent tin complexes.

The reaction of $SnCl_2$ with 1 equiv of $\{Li(C_6H_2\text{-}2,4,6\text{-}Cy_3)\cdot OEt_2\}_2$ in diethyl ether results in the precipitation of a bright-red powder. Extraction of the powder in toluene and recrystallization of the residue from a 1:2 mixture of hexanes/toluene at ca. −30 °C affords cherry-red crystals of $\{Sn(C_6H_2\text{-}2,4,6\text{-}Cy_3)_2\}_2$ (**1**), the structure of which is shown in Figure 1. The distannene has the folded, trans-pyramidalized geometry (sum of angles at tin = 343.67(15)°) and trans-bending angle (36.83(9)°) typical of most distannenes,[9] with a slight twist angle of 8.28(10)° between the C−Sn−C planes. Thus, in agreement with calculated Kohn−Sham orbitals of **1** (Figure 2a) and the natural bonding orbital (NBO) analysis (cf. Figure 2b), the structural parameters of **1** are consistent with a weak bond between the tin atoms.[10] Despite the bulk of the ligands, **1** displays a short Sn−Sn separation of 2.7011(7) Å. In addition, there are several close interligand H−H contacts involving the cyclohexyl rings across the Sn−Sn bond, suggesting a high degree of LD attraction between SnR_2 units. Among structurally characterized $(SnR_2)_2$ complexes (excluding cyclic distannenes), only the distannene $\{Sn(Si^tBu_2Me)_2\}_2$

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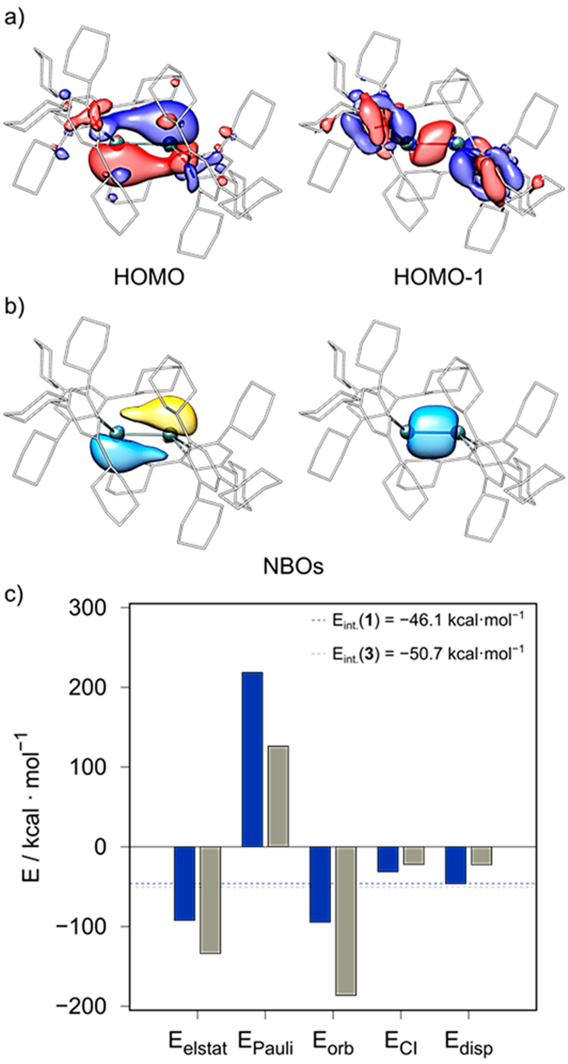

Figure 2. (a) Selected Kohn−Sham orbitals and (b) natural bonding orbitals (isosurface value = 0.05 au) for **1**. (c) EDA for **1** (blue) and {Sn(Si^{t}Bu$_2$Me)$_2$}$_2$ (**3**, gray) at the BLYP-D4/def2-QZVP//r2SCAN-3c level of theory. The dashed lines represent the overall interaction energies of the corresponding stannylene fragments SnR$_2$. Isosurface value = 0.03 au.

(**3**) reported by Sekiguchi and co-workers in 2004 possesses a shorter Sn−Sn bond of 2.6679(8) Å.[13] That complex is the only distannene known to remain dimeric in solution at ambient (or higher) temperature as evidenced by its ^{119}Sn NMR chemical shift and its reactivity with CCl$_4$ and phenylacetylene to give {Sn(Cl)R$_2$}$_2$ or a four-membered [2 + 2] cycloaddition product. However, the tin atoms in that molecule are essentially planar-coordinated, and the Si−Sn−Si planes have a torsion angle of ca. 45°. Thus, the shorter Sn−Sn bond and its high strength can be attributed at least in part to the presence of a covalent σ bond and a twisted π bond between two triplet state tin units. In contrast, the trans-pyramidal structure of {Sn(C$_6$H$_2$-2,4,6-Cy$_3$)$_2$}$_2$ suggests weak Sn−Sn bonding like that observed in most other distannenes so that any unusually strong interaction between its SnR$_2$ units must originate from another source.

A computational study at the B3LYP-D4/def2-QZVP +COSMO-RS/r^{2}SCAN-3c(COSMO) level[30−34] (SI) of {Sn(C$_6$H$_2$-2,4,6-Cy$_3$)$_2$}$_2$ indicated that, when dispersion effects are excluded, the monomeric stannylene Sn(C$_6$H$_2$-2,4,6-Cy$_3$)$_2$ is favored (ΔG_{dimer} = +31.9 kcal mol^{-1}). In contrast, including LD effects in the calculations using the accurate D4 model shows that the dimer is clearly favored, with a ΔG_{dimer} of −6.1 kcal mol^{-1} (ΔH_{dimer} = −24.5 kcal mol^{-1}). For **3**, these values are +3.1 and −13.5 kcal mol^{-1}, respectively, highlighting the unusually large impact of LD interactions in **1**. The importance of LD contributions is further supported by an energy decomposition analysis of **1** (Figure 2c). For **1**, a comparably small E_{orb} component is observed, while the E_{int} to E_{disp} ratio amounts to 1.0. Neglecting the dispersion component results in a slightly repulsive interaction energy of 0.3 kcal mol^{-1}, thus underlining the crucial role of LD. For **3**, the interaction energy is dominated by E_{orb}, yielding a small E_{disp}/E_{int} = 0.4. Furthermore, for **3** the E_{int} value is negative by −28.1 kcal mol^{-1} without the inclusion of dispersion effects, indicating the dominant role of the stronger tin−tin bond.

The magnitude of ΔG_{dimer} for **1** suggests that this complex should remain dimeric in solution even at elevated temperature (at 300 K, a ΔG value of ca. −6 kcal mol^{-1} indicates an equilibrium constant of ca. 10^4 favoring the dimer). The ^{119}Sn NMR chemical shift of distannene **1** was predicted in our computational study to be δ = 388.2 ppm (SO-ZORA-revPBE(COSMO)/ZORA/TZP).[35−37] This agrees well with the experimental spectrum of distannene **1** at room temperature, which displayed a single resonance at δ = 361.3 ppm. Given that ^{119}Sn signals appear over a very wide range (ca. −2000 to +3000 ppm), this signal is in a region similar to the reported chemical shifts of SnR$_2$ complexes that possess a Sn−Sn bond in solution (cf. {Sn(SiBu$^t_2$Me)$_2$}$_2$, δ = 630.7 ppm; {Sn(C$_6$H$_2$-2,4,6-^{i}Pr$_3$)$_2$}$_2$, δ = 427 ppm, which remains dimeric in solution only at low temperatures of ca. −70 °C; see Wrackmeyer's reviews for a general overview of the topic).[14,38−40] At 350 K, this signal shifts slightly downfield to 369.3 ppm, but no signal for the monomer was detected in the range of 1250 to 3750 ppm (the chemical shift of the monomer was calculated to be δ = 2569 ppm), indicating that complex **1** remains dimeric in solution even at elevated temperatures, in agreement with the theoretical result. Additionally, a variable-temperature UV−visible spectroscopy study over the temperature range of −10 to 100 °C showed only a single absorbance in the visible region at 505 nm. However, despite several attempts and a variety of conditions, no new products were isolated from its reactions with excesses of either phenylacetylene or ethylene. The low reactivity of {Sn(C$_6$H$_2$-2,4,6-Cy$_3$)$_2$}$_2$ with respect to these reagents is consistent with high steric congestion around the tin atoms. A space-filling model of the structure (Figure 3) clearly shows that the tin atoms are almost wholly obscured in the dimer.

In contrast to the high stability of {Sn(C$_6$H$_2$-2,4,6-Cy$_3$)$_2$}$_2$ (**1**), the use of the 2,4,6-triphenylphenyl ligand, which is less bulky but has a configuration similar to that of the −C$_6$H$_2$-2,4,6-Cy$_3$ ligand used in **1**, gives very different results. In a preparation similar to that of {Sn(C$_6$H$_2$-2,4,6-Cy$_3$)$_2$}$_2$, SnCl$_2$ was treated with 2 equiv of Li(C$_6$H$_2$-2,4,6-Ph$_3$)·(OEt$_2$)$_2$[29] in diethyl ether. After this mixture was stirred overnight, a large amount of red powder was precipitated. Extraction of the red material in toluene and recrystallization of a concentrated toluene solution layered with diethyl ether gave large, red crystals of Sn(C$_6$H$_2$-2,4,6-Ph$_3$)$_2$ (**2**) in moderate yield. Despite the reduced bulk of the ligand, a structural study showed that it is monomeric in the solid state (Figure 4). Its molecular structure is broadly similar to that of its lead analogue, which was reported by Robinson in 2005.[41] Its C−Sn−C angle

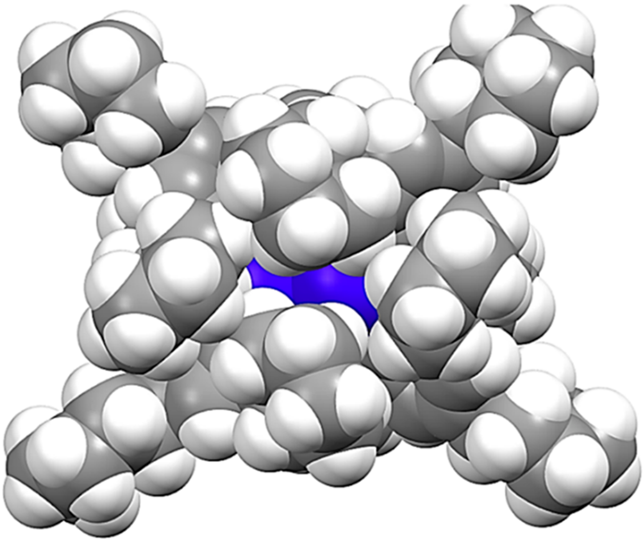

Figure 3. Space-filling model of **1** with tin atoms shown in dark blue. Spheres are shown at 100% of the van der Waals radius of the respective element.

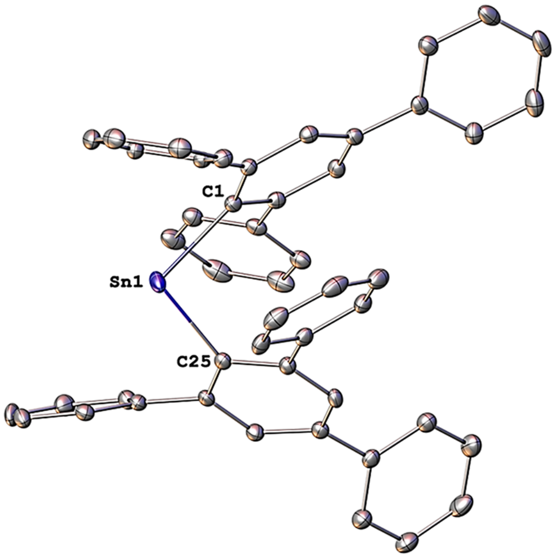

Figure 4. Molecular structure of **2** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms are not shown. Selected bond distances (Å) and angles (deg): Sn1−C1:2.222(3), Sn2−C25:2.233(3), and C1−Sn1−C25:96.36(9).

(96.36(9)°) is notably sharp and is comparable to that of the stannylene Sn{C_6H_3-2,6-(C_6H_2-2,4,6-^{i}Pr_3)$_2$}(Ph) (C−Sn−C angle = 98.86°).[42] The shortest Sn−Sn distance in the crystal structure is 7.8870(9) Å, confirming the monomeric structure. Sn(C_6H_2-2,4,6-Ph_3)$_2$ is unstable in solution, and attempts to redissolve it result in an immediate color change from red to brown and the deposition of an insoluble solid of currently unknown composition (likely polymeric,[43] see the SI for spectra). Computational studies for **2** showed that the formation of the monomeric stannylene is favored over the distannene, even when LD effects are considered (ΔG_{dimer} = +8.8 kcal mol^{-1}). Although few further details are currently available due to its instability, its monomeric structure underlines the importance of the stabilizing effects of LD attraction in **1**, and in distannenes generally.

In conclusion, the trans-pyramidalized distannene {Sn(C_6H_2-2,4,6-Cy_3)$_2$}$_2$ (**1**) was shown to remain dimeric in solution over a wide range of temperatures. Its enhanced thermodynamic stability compared to that of other distannenes was determined computationally to be due to London dispersion (LD) attraction between SnR_2 units. Unlike the previously reported solution-stable distannene {Sn($SiBu^t_2Me$)$_2$}$_2$, which possesses a comparably strong interaction between the tin atoms, the strong dimerization in **1** is dominated by the presence of these LD attractions since its trans bent structure indicates only a weak nonclassical double bond between the tin atoms, in agreement with the NBO analysis. In contrast, using the less bulky 2,4,6-triphenylphenyl ligand afforded the monomeric stannylene Sn(C_6H_2-2,4,6-Ph_3)$_2$ (**2**), which was shown to be unstable in solution. The instability of monomeric **2** underscores the importance of LD attraction in stabilizing **1** via its dispersion effect donor ligand −C_6H_2-2,4,6-Cy_3.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c09976.

> Spectra (NMR, infrared, and UV−vis), crystallographic data, computational details, coordinates of the optimized structures, and photographs of the materials (PDF)

Accession Codes

CCDC 2091040, 2098934, 2106457, and 2108933 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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