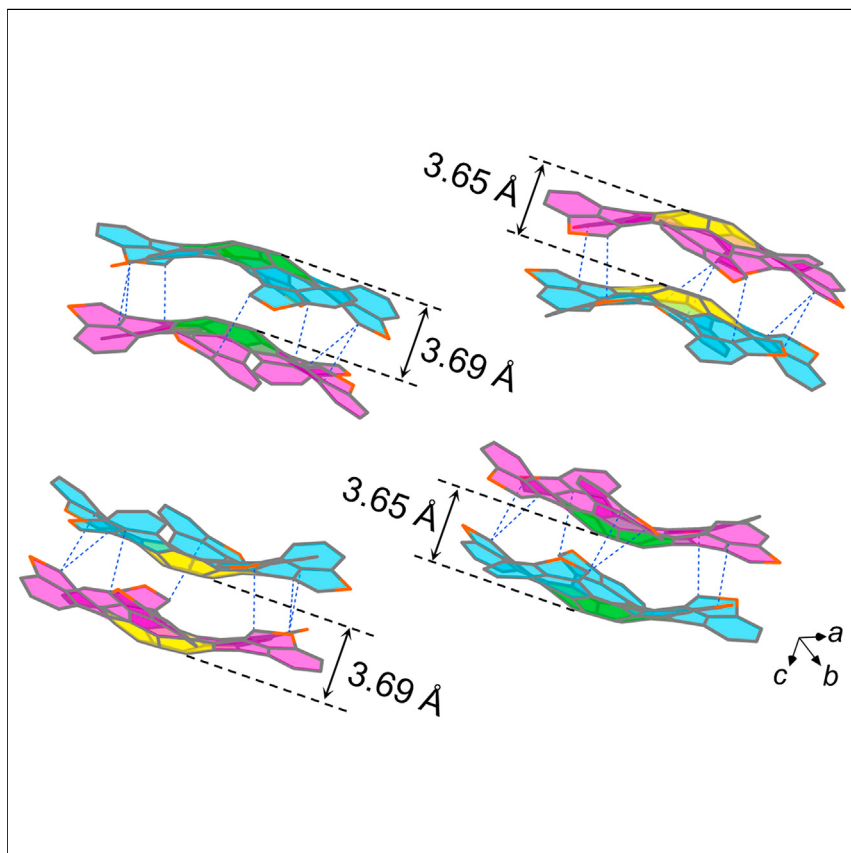


Article

Chiral stacks of a curved nanographene



This study describes the effect of *peri*-annulations on the molecular properties of nanographenes. In contrast to *ortho*-annulated structures and archetypical planar nanographenes, the *peri*-annulated chiral structures exhibit a significant red shift in the absorption and emission spectra, lower band gap, and propensity to form discrete bilayer and multilayer nanostructures.

Zhongbo Zhang, Dániel Csókás,
Israel Fernández, Mihaiela C.
Stuparu

mstuparu@ntu.edu.sg

Highlights

Extension of the zigzag edges, *peri*-annulations, is established in nanographenes

Peri-annulated nanographene exhibits superior electronic and assembling properties

Peri-annulated nanographenes can form multilayered chiral nanostructures

The molecular graphene bilayer is stable in solution, solid state, and gas phase



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Article

Chiral stacks of a curved nanographene

Zhongbo Zhang,¹ Dániel Csókás,² Israel Fernández,³ and Mihaiela C. Stuparu^{1,4,5,*}

SUMMARY

Despite enormous advances in the edge extension chemistry of nanographenes, examples of *peri*-annulations and the knowledge of their effect on molecular properties remain scarce. Here, we show the synthesis of a curved C₆₀S₅ nanographene comprising quintuple [5]thiahelices arranged in a C₅-symmetric fashion on the zigzag edge (L-region) of a bowl-shaped corannulene core. The synthesis is achieved with the help of Stille coupling, alkynyl thiolation, sulfide/aryne cyclization, and direct arylation reactions. The prepared bowl-helix chiral structure absorbs and emits in the visible and near-IR regions. It assembles into persistent molecular bilayer graphene stacks in solution, solid state, and gas phase. The concave cavities of the supramolecular dimers can recognize the convex surfaces of fullerene C₆₀ through shape complementarity and π - π stacking interactions in the solid state. A properties comparison with *ortho*-annulated analogs and archetypical nanographenes indicates the superiority of *peri*-annulations in the design of molecular graphenes.

INTRODUCTION

Annulation of aromatic rings to a polycyclic aromatic hydrocarbon core represents a practical strategy toward controlled growth of nanographenes.^{1–4} These annulations can occur at the bay-region (concave armchair edges), K-region (convex armchair edges), and L-region (zigzag edges) of the core molecule. Among these, aromatic area extensions at the bay-region (*ortho-ortho*-annulation) and K-region (*ortho*-annulation) are ubiquitous.^{1–4} Examples of edge extension through the zigzag edge (*peri*-annulation) are comparatively rare.^{5–8} Their significance, however, can be gauged by the rylene series, which is accessed upon zigzag edge extension of naphthylenes.^{9,10} They are more stable than acenes and exhibit a lower optical band gap in comparison with the fully benzenoid polycyclic aromatic hydrocarbons.¹¹ Thus, *peri*-annulations constitute an important yet relatively underexplored mechanism for nanographene formation.

Nanographenes are molecular analogs of graphene. Their discrete multilayered structures, analogous to graphene's layered structure, are anticipated to have properties distinct from the monolayer structure.^{12,13} Thus, molecularly layered graphenes are receiving increased attention. However, assembling nanographene multilayers is a challenging task. Covalent systems in which a tether links nanographene fragments cannot be considered true multilayers as the linker becomes the critical factor in governing the interactions between the layers and their properties (which is absent in graphene bilayers).^{14–18} Non-covalent systems with low stability and a propensity for higher order assembly and aggregation (being non-discrete) also do not represent molecular bilayers. Thus, supramolecular layered structures of nanographenes having a discrete number of layers and stability in solution, as

THE BIGGER PICTURE

Nanographenes are molecularly precise fragments of graphene with excellent optoelectronic properties and potential applications in future technologies. Thus, the design and synthesis of new nanographene molecules is currently a major research endeavor. The main synthetic strategy to achieve this goal relies on the edge extension of small aromatic molecules. The extension chemistry, however, is mostly restricted to *ortho*-annulations (extension of the bay-region and K-region). In this work, we show the importance of *peri*-annulations, extension of the zigzag edges, in nanographene research. We show that *peri*-annulations endow a nanographene molecule with superior electronic properties and the capacity to assemble into discrete multilayer carbon nanostructures.



established by Tan and coworkers,¹⁹ remains severely restricted to just a few examples.^{19–27}

In this work, we establish quintuple *peri*-annulations on a bowl-shaped corannulene core^{28–30} and show their remarkable effect on electronic properties and self-assembly behavior. To achieve this, quintuple [5]thiahelices are installed on the core fragment in a C_5 -symmetric fashion. The resulting bowl-helix chiral structure assembles into a stable bilayer structure in solution, solid state, and gas phase. The assembly can be extended to include four layers of nanographenes upon molecular recognition with fullerene C_{60} . By contrast, similar systems with 5-fold *ortho*-annulations do not exhibit such self-assembling characteristics.^{31–34} Furthermore, *peri*-annulations lead to a large red shift in absorption and emission spectra as compared with *ortho*-annulated analogs. A comparison with archetypical planar nanographenes indicates a significantly lower optical band gap for the *peri*-annulated, curved structure.¹¹ In essence, this work underlines the importance of *peri*-annulations on the structure and properties of molecular graphene materials.

RESULTS AND DISCUSSION

The synthesis of **4** required four synthetic steps (Figure 1). First, a common precursor in corannulene chemistry, *sym*-pentachlorocorannulene^{35,36} was subjected to a palladium-catalyzed ethynylation reaction with the help of trimethyltin-substituted trimethylsilylacetylene.³⁷ The pentakis(trimethylsilylethynyl)corannulene (**1**) was then subjected to the removal of silyl groups with the help of tetrabutylammonium fluoride followed by 5-fold copper-catalyzed thiolation to obtain **2** in an isolated yield of 27% (over two steps).³⁸ A cyclization between the alkynyl sulfide moieties in compound **2** and aryne precursor 2-bromo-4-*tert*-butyl-6-(trimethylsilyl)phenyl triflate³⁹ furnished the benzothiophene-substituted corannulene **3** in 18% isolated yield.⁴⁰ Finally, intramolecular cyclization through 5-fold palladium-catalyzed direct arylation under microwave conditions yielded compound **4** in an isolated yield of 11%.⁴¹ In the present system, *ortho*-annulation would have led to the formation of a five-membered ring, while *peri*-annulation led to the formation of a six-membered ring. It is likely that a comparatively lower ring-strain during the formation of a six-membered ring resulted in the observed regio-selectivity toward *peri*-annulation. Moreover, replacing **3** with its chloride analog also led to a successful intramolecular cyclization reaction, albeit with a lower isolated yield of **4** (4%). In **4**, the attachment of the benzothiophene moieties to the corannulene core is through flank (*L*-region) bonds. In all the other known corannulene-core quintuple helices, the attachment of the helix fragments to the core takes place through the rim bonds (*K*-region).^{31–34}

Considering helical and bowl chirality elements in **4**,^{42–46} sixteen stereoisomers consisting of eight pairs of enantiomers can be envisioned (Figures 2 and S1). To describe these, Figure 2A depicts the nomenclature rules that are inspired by the earlier work from Petrukhina, albeit with the addition of letters *X* and *V* to clearly distinguish between bowl chirality element from the helical-chirality (which is defined by letters *P* and *M*).⁴⁷ Single crystals could be obtained readily to shed more light on these aspects with the help of X-ray crystallography. In a unit cell, we observed two types of diastereomeric monomers, each consisting of one enantiomer pair, namely [*V*,*MMMMM*], [*X*,*PPPPP*], and [*V*,*PPPPP*], [*X*,*MMMMM*] (Figure 3). However, each enantiomer displayed two distinct conformations distinguished by characteristic torsional angles and bowl depths, which is likely due to the particular intermolecular interactions within the crystal lattice (Figures S2–S5; Tables S1–S5). Thus, the monomers [*V*,*MMMMM*] — [*X*,*PPPPP*] and

¹School of Chemistry, Chemical Engineering and Biotechnology, Nanyang Technological University, 21 Nanyang Link, 637371 Singapore, Singapore

²Institute of Organic Chemistry, HUN-REN Research Centre for Natural Sciences, Magyar tudósok körútja 2, 1117 Budapest, Hungary

³Departamento de Química Orgánica I, Centro de Innovación en Química Avanzada (ORFEO-CINQA), Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

⁴National Institute for Research and Development of Isotopic and Molecular Technologies—INCDTIM, 67-103 Donat Street, 400293 Cluj-Napoca, Romania

⁵Lead contact

*Correspondence: mstuparu@ntu.edu.sg
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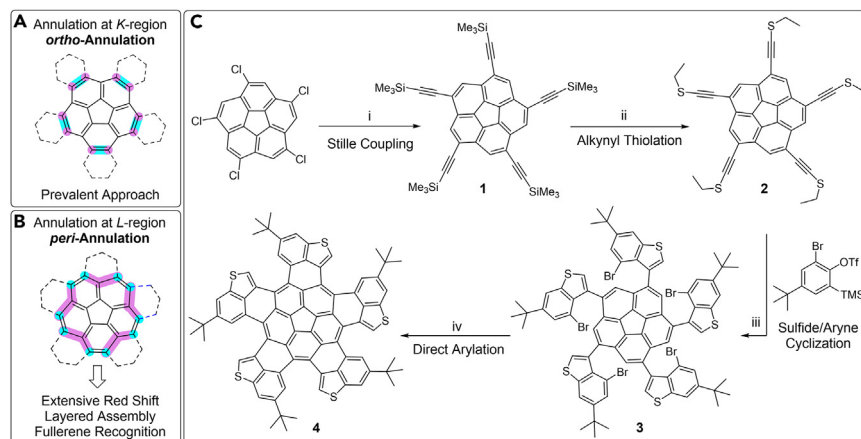


Figure 1. Annulation chemistries on a corannulene core and synthesis of 4

(A) Annulation at K-region typically used in the synthesis of curved nanographenes.

(B) Quintuple *peri*-annulations on the zigzag edge of corannulene as established in this work.

(C) Reagents and conditions. (i) Trimethyl((trimethylstannyl)ethynyl)silane (8.0 equiv), Pd(OAc)₂ (0.5 equiv), *t*-BuOK (1.0 equiv), *i*Pr·HCl (1.0 equiv), DME, 110°C, 3 days. (ii) *n*-Bu₄NF (10.0 equiv), THF, rt, 1 h; *S*-ethyl 4-methylbenzenesulfonothioate (15.0 equiv), CuI (0.60 equiv), Xantphos (0.72 equiv), K₂CO₃ (7.5 equiv), DMSO, RT, 3 days. (iii) 2-Bromo-4-(*tert*-butyl)-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (60.0 equiv), CsF (90.0 equiv), DME/MeCN, 80°C, 7 days. (iv) Pd(MeCN)₂Cl₂ (5.0 equiv), PPh₃ (2.5 equiv), DBN, MeCN, 170°C, microwave, 1 h. Abbreviations: THF, tetrahydrofuran; DMSO, dimethylsulfoxide; DME, dimethoxyethane; DBN, 1,5-diazabicyclo [4.3.0]non-5-ene; MeCN, acetonitrile.

[*V*,*PPPPP*] --- [*X*,*MMMMM*] are two sets of enantiomer pairs, and the notations I and II represent the two distinct conformations observed in the crystal structure. Therefore, the molecules identified in the solid state are [*V*,*MMMMM*]-I, [*X*,*PPPPP*]-I, [*V*,*PPPPP*]-I, [*X*,*MMMMM*]-I, [*V*,*MMMMM*]-II, [*X*,*PPPPP*]-II, [*V*,*PPPPP*]-II, and [*X*,*MMMMM*]-II. The eight molecules combined to form four dimers in total, which can be classified into two diastereomeric groups: [*X*,*MMMMM*]-I $\subset$ [*X*,*PPPPP*]-I, [*V*,*PPPPP*]-I $\subset$ [*V*,*MMMMM*]-I, [*X*,*MMMMM*]-II $\subset$ [*X*,*PPPPP*]-II, and [*V*,*PPPPP*]-II $\subset$ [*V*,*MMMMM*]-II. Dimers [*X*,*MMMMM*]-I $\subset$ [*X*,*PPPPP*]-I and [*V*,*PPPPP*]-I $\subset$ [*V*,*MMMMM*]-I showed π - π distance of 3.65 Å. Whereas dimers [*X*,*MMMMM*]-II $\subset$ [*X*,*PPPPP*]-II and [*V*,*PPPPP*]-II $\subset$ [*V*,*MMMMM*]-II showed π - π distance of 3.69 Å. These dimers are packed in two-dimensional (2D) arrays; dimers with *V*-type of bowls and dimers with *X*-type of bowls packed in a row by adopting concave-concave and convex-convex packing arrangements, respectively. From the top view of 4, the radius of its conjugation length is 7.5 Å (Figure S6). From the side view of 4, the depth of corannulene and its conjugation rim are 0.76 and 2.31 Å, respectively (Figure S6).

Solution studies were then pursued. In ¹H NMR, two sets of proton signals (labeled A and B) with an integral ratio of 1:1 could be observed for 4 at 298 K in deuterated chloroform and benzene (Figures 4A and S7). In deuterated toluene, chlorobenzene, 1,2-dichlorobenzene, and nitrobenzene, three sets of proton resonances (labeled A, B, and C) could be observed with integral ratios of 1:1:0.16, 1:1:0.60, 1:1:1.25, and 1:1:1.46, respectively, at 298 K. In deuterated dichloromethane and tetrachloroethane, the proton resonances sharpen only after decreasing the temperature, thus suggesting a low energy barrier of transition states for interconversion of conformations in these two solvents (Figures S8 and S9). In dichloromethane, integral ratios of 1:1 are observed for A and B at 238 K, whereas in tetrachloroethane, A, B, and C could be observed with an integral ratio of 1:1:0.4 at 258 K. 2D NOESY and ROESY spectra shows intramolecular nuclear

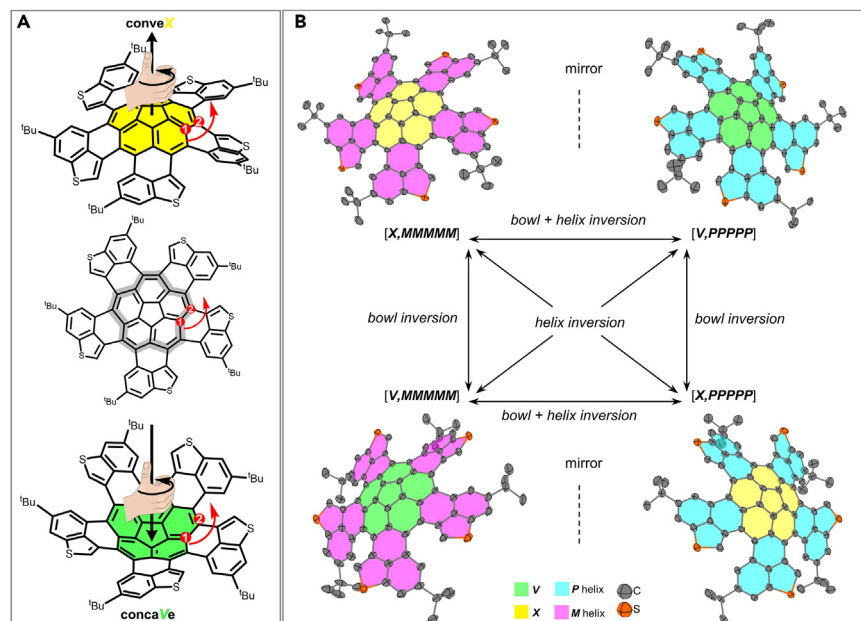


Figure 2. Conformational aspects of 4

(A) Nomenclature of bowl chirality as adopted in this work. Identify the bowl unit and establish priorities as per the Cahn-Ingold-Prelog (CIP) rules (middle). When the fingers of the curled right-hand follow the direction of CIP priority and the thumb points toward the direction of bowl convex, the bowl chirality is defined as **X** (top). When the thumb points in the opposite direction of bowl convex, the bowl chirality is defined as **V** (bottom).

(B) **[X,MMMM]** and **[V,PPPP]** are enantiomers, and **[X,PPPP]** and **[V,MMMM]** are enantiomers. These enantiomers can interconvert through bowl and helix inversion processes.

Overhauser effect between different sets of proton signals (A, B, and C), indicating that the molecules are very close in space ($\leq 5 \text{ \AA}$) (Figures S10–S14). Diffusion-ordered spectroscopy (DOSY) showed the same diffusion band for A and B (Figures S15, S16, and S17). Proton signals C showed the same diffusion band but a higher diffusion coefficient than A and B. This suggested that signals A and B derive from the species having the same size, whereas signals C result from the species, which has smaller size than A and B. Variable temperature NMR indicated merging and broadening of the signals, indicative of fast conformational changes (helix and bowl inversion) at higher temperatures ($>328 \text{ K}$) for chloroform, benzene, toluene, chlorobenzene, 1,2-dichlorobenzene, and nitrobenzene (Figures S18–S21). For variable concentration NMR, in deuterated benzene at 298 K , the integral ratio of signals C increased gradually from less than 3% to over 95% with the concentration decreasing from 5.08×10^{-3} to $8.46 \times 10^{-6} \text{ mol/L}$ while the integral ratio of signals A and B remained constant at 1:1 (Figures S22 and S23). In deuterated chloroform at 298 K , the integral ratio of signals C increased gradually from less than 3% to 78% with the concentration decreasing from 5.08×10^{-3} to $8.46 \times 10^{-6} \text{ mol/L}$ (Figure S24). Once again, the integral ratio of signals A and B remained constant at 1:1. In deuterated chlorobenzene at 298 K , the integral ratio of signals C increased gradually from 13% to over 95% with the concentration decreasing from $1.52 \times 10^{-2} \text{ mol/L}$ (saturated) to $4.23 \times 10^{-5} \text{ mol/L}$, and the integral ratio of signals A and B remained constant at 1:1 (Figure S25).

From these results, it is reasonable to assume that signals A and B are proton resonances of two pairs of C_5 -symmetric enantiomers (**[V,PPPP]** and **[X,MMMM]**) and (**[X,PPPP]** and **[V,MMMM]**) in the dimeric form. Whereas signals C are proton

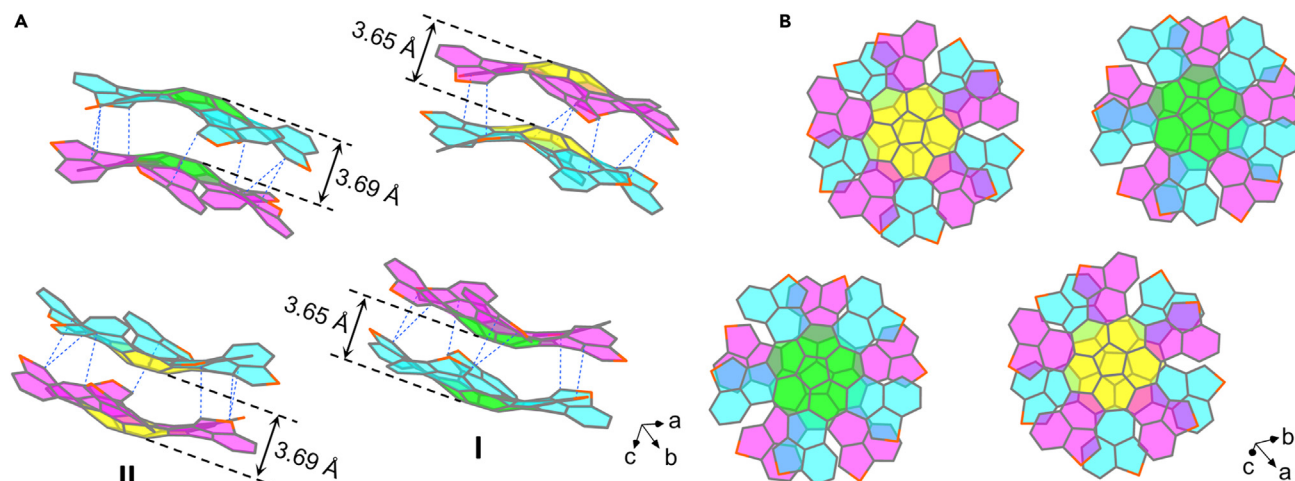


Figure 3. Single crystal structure of 4

tert-Butyl groups, hydrogen atoms, and solvent molecules are omitted for clarity. The π - π distance is defined by the distance between the mean planes of the central five-member rings.

(A) Side view of the molecular packing in the crystalline state of 4. Aromatic stacking interactions are shown with blue dashed lines.

(B) Top view of the molecular packing in crystalline state of 4.

resonances of C_5 -symmetric enantiomer ([V,PPPPP] and [X,MMMMM]) in the monomer states. The ratio of signals A and B is always constant in a 1:1 ratio, irrespective of the conditions, and only the content of C is changed upon changing the nature of the solvent and concentration. Solvents of low dielectric constants favor the dimerization even at low concentrations and high temperatures.

Encouraged by the results thus far, high-resolution atmospheric pressure chemical ionization mass spectrometry (HR-APCI-MS) study was carried out. This is a soft ionization technique that hinders molecular fragmentation. This study detected the dimeric species ($[2M+H]^+$) of 4 ($C_{160}H_{121}S_{10}$) at 2,361.6663 in the gas phase and corroborated the solution and solid-state studies in concluding the persistent nature of the supramolecular dimeric species (Figure S25).

Subsequently, fullerene C_{60} was used as a supramolecular glue to bring two bilayers together and form larger nanostructures in the solid state. To this end, co-crystals were grown and studied with the help of X-ray crystallography (Figure 6A).^{48,49} In the co-crystals of $4 \subset C_{60}$, eight different molecules of 4 in four conformations like 4 were observed with slight variations in the torsional angles and bowl depths (Figures S26–S29; Tables S6–S10). In the long-range packing of $4 \subset C_{60}$, similar dimers were observed as in the crystal of 4. One C_{60} molecule coordinated with two dimers, which exhibited the same bowl chirality and formed two types of complexes: complex X ([X,MMMMM]-I $\subset$ [X,PPPPP]-I $\subset C_{60}$ $\Rightarrow$ [X,PPPPP]-II $\supset$ [X,MMMMM]-II) and complex V ([V,PPPPP]-I $\subset$ [V,MMMMM]-I $\subset C_{60}$ $\Rightarrow$ [V,MMMMM]-II $\supset$ [V,PPPPP]-II), whereas layers of X and V packed in an alternating fashion in the single crystal.

Variable temperature NMR enabled understanding the thermodynamics of bilayer formation. For this, at a certain temperature and in a certain solvent, the concentration of the monomer and the dimer was determined and converted into the association constant with the help of the equation $K_a = [4_{\text{dimer}}]/[4_{\text{monomer}}]^2$ (Tables S11–S14; Figures S30–S33).²⁷ These data indicated that the association strength between the two layers is inversely proportional to the dielectric constant of the solvent and the temperature. In chloroform, a solvent that favors dimerization, the association

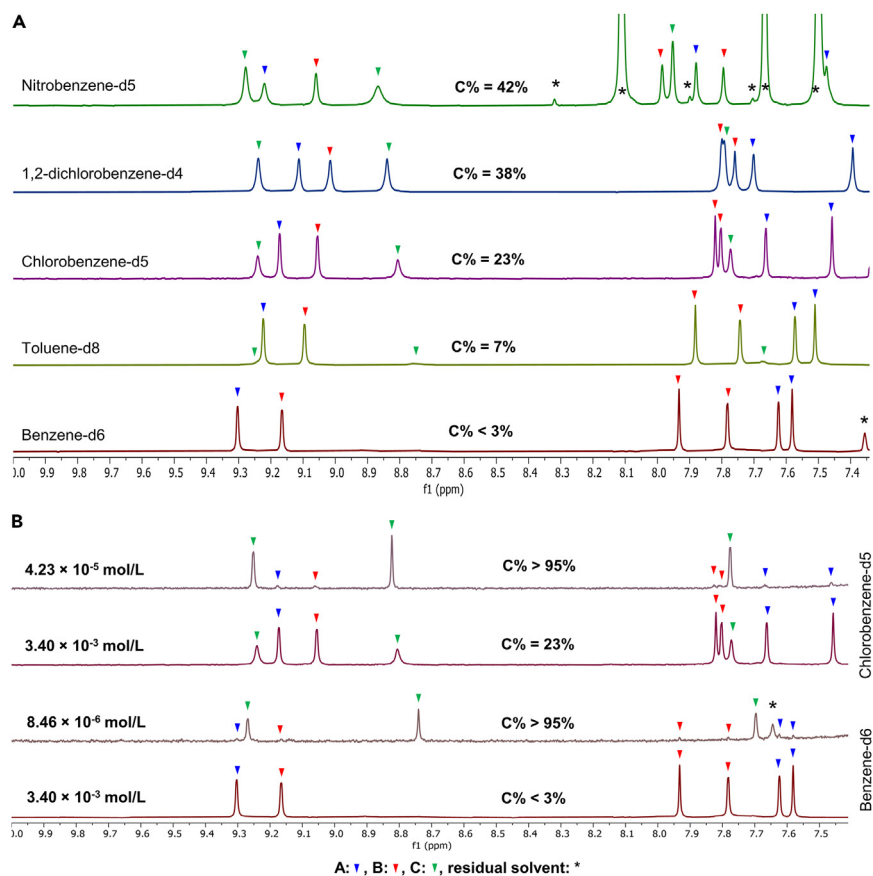


Figure 4. NMR study

(A) Expanded ¹H NMR of **4** in different deuterated solvents with a concentration of 3.40 × 10⁻³ mol/L at 298 K.

(B) Expanded variable concentration ¹H NMR of **4** in deuterated chlorobenzene (with a concentration of 3.40 × 10⁻³ mol/L and 4.23 × 10⁻⁵ mol/L) and deuterated benzene (with a concentration of 3.40 × 10⁻³ mol/L and 8.46 × 10⁻⁶ mol/L) at 298 K.

constant is calculated to be 4.3 × 10⁴ M⁻¹ at room temperature. In chlorobenzene, dichlorobenzene, and nitrobenzene, the association constant is calculated to be 1,556, 647, and 319 M⁻¹, respectively, at room temperature. In each solvent, the association constant increased with a lowering of the temperature, and vice versa. A van't Hoff analysis of this data indicated the bilayer formation to be a spontaneous process.

Density functional theory (DFT) calculations were carried out to gain more insights into the conformational (Figures S34–S41) and dimerization aspects (Figures 6B and S42). These calculations helped in quantifying the influence of π -extension and *tert*-butyl-substitution on the stability of the nanographene bilayer. Based on the relative electronic energies, the benzothiophene moieties appear to contribute to the stability of the dimeric form by about 50 kcal/mol, implying that one pair of benzothiophenes increases the stability by 10 kcal/mol. The contribution of *tert*-butyl groups to the dimer stability is comparatively modest as the difference between non-*tert*-butyl-substituted derivative of **4** and dimer of **4** in electronic energy is only ca. 13.0 kcal/mol. This implies that the stability is influenced by approximately 2.6 kcal/mol by each pair of *tert*-butyl groups. These interactions are apparent in the

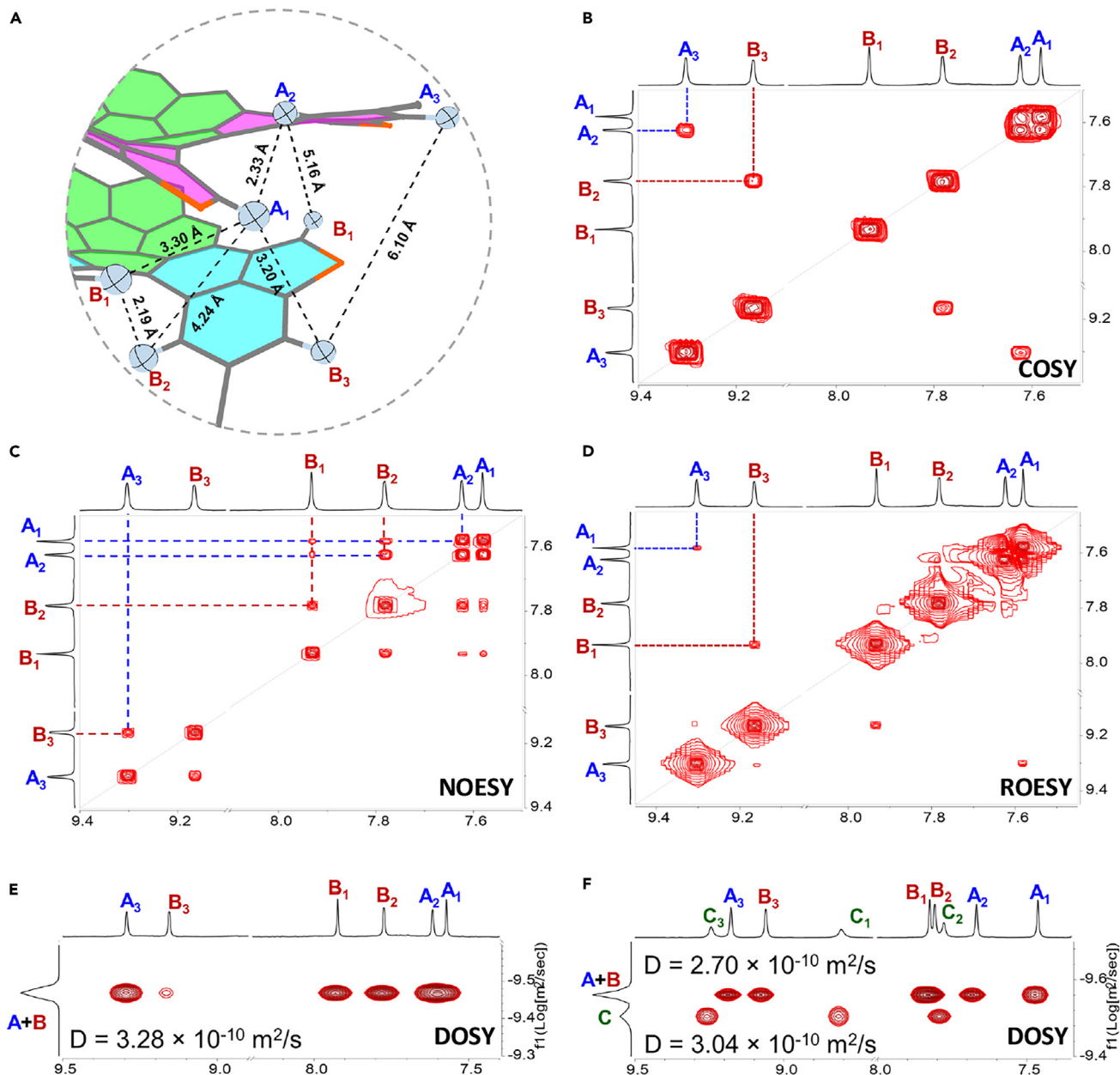


Figure 5. 2D NMR study

(A) Distances among the hydrogen atoms in the molecular bilayer graphene as observed in the crystalline state.

(B) Expanded ¹H-¹H COSY NMR of 4 in deuterated benzene.

(C) Expanded NOESY NMR of 4 in deuterated benzene.

(D) Expanded ROESY NMR of 4 in deuterated benzene. A concentration of $3.40 \times 10^{-3} \text{ mol/L}$ at 298 K is used for all experiments.

(E) Diffusion-ordered spectroscopy (DOSY) spectra of 4 in deuterated benzene.

(F) DOSY spectra of 4 in deuterated chlorobenzene. A concentration of $3.40 \times 10^{-3} \text{ mol/L}$ at 298 K is used for DOSY experiments.

non-covalent interactions (NCIs) plot constructed for the bilayer structure (Figure 6C).⁵⁰

The UV-vis absorption and emission characteristic of 4 was investigated in chlorobenzene at room temperature and at a concentration at which NMR studies (Figure S24) indicate presence of only the monomer (Figures 7 and S43-S45;

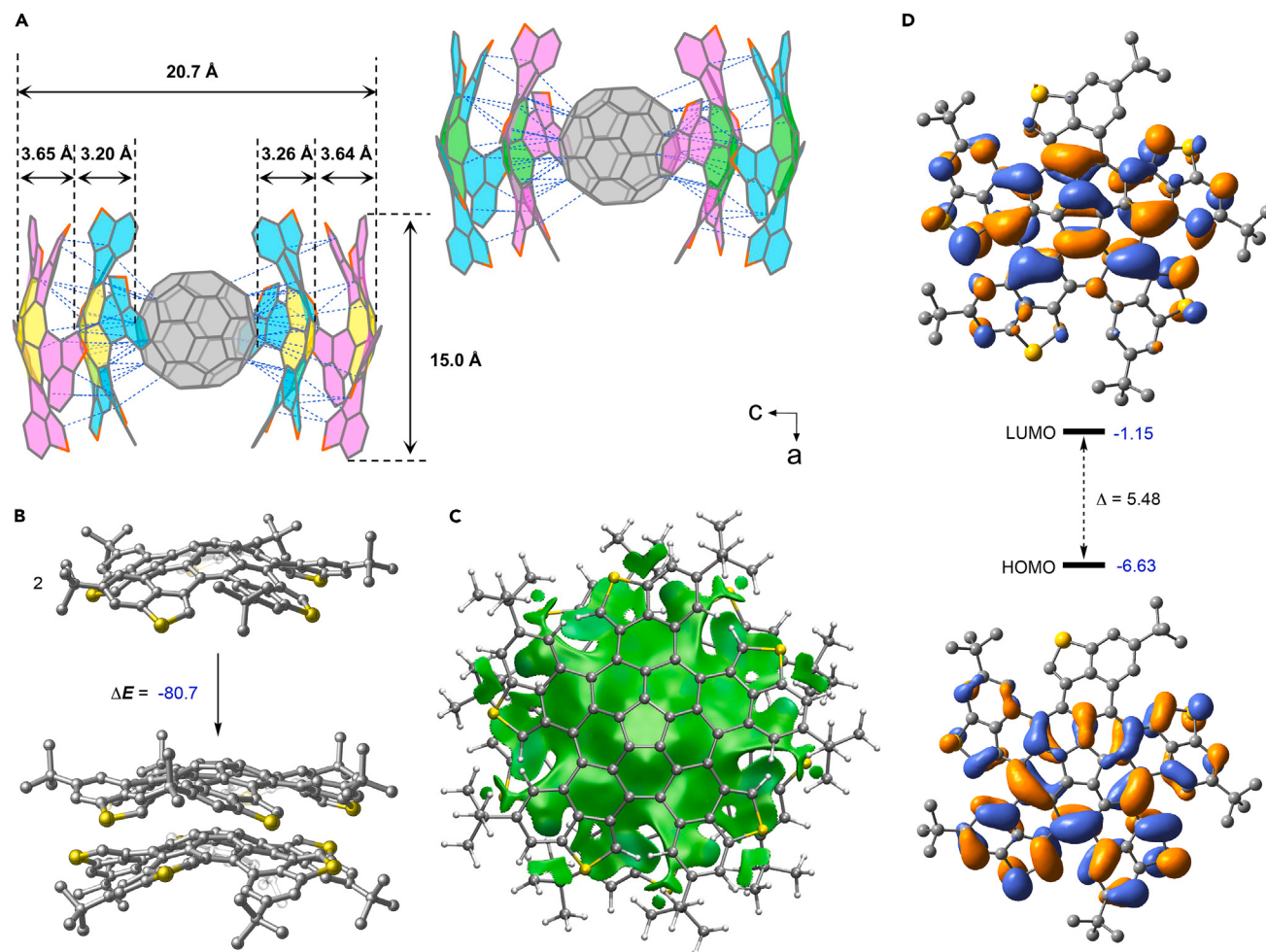


Figure 6. Multilayer assembly of 4 and computational studies

(A) Side view of the molecular packing and aromatic stacking interactions (blue dash lines) of **4**=C₆₀ in single crystalline state. *tert*-Butyl groups, hydrogen atoms, and solvent molecules are omitted for clarity.

(B) Computed energetics of dimerization nanographene **4** and its dimer. The relative electronic energies (ΔE) were calculated at the ω B97X-D/Def2TZVPP level of theory. The ΔE is given in kcal/mol with respect to the most stable monomeric form.

(C) Stabilizing interactions are represented by a green surface in NCI plot of the bilayer structure of **4**.

(D) Frontier molecular orbitals for **4**. Orbital energies (highlighted in blue) and the HOMO-LUMO energy gaps (Δ) are given in eV.

Table S15). The absorption maximum of **4** appears at 573 nm with absorption tailing up to 850 nm. The emission spectrum displays maximum emission at 684 nm with a shoulder at 746 nm. The fluorescence quantum yield is observed to be low ($\Phi \leq 0.1\%$). The optical band gap from the absorption data can be calculated to be 1.79 eV. A comparison can be made to quintuple-helicene systems (**5**–**8**) synthesized through *ortho*-annulation.^{31–34} In **7**, nitrogen atoms are directly placed onto the core, which are expected to bring a significant red shift due to their electron-donating character.³³ In **8**, a vast π -system (120 π -electrons) is created with the help of *ortho*-annulation with rylene dyes.³⁴ Yet, these systems exhibit absorption maxima below 500 nm. A second comparison can be made with archetypical nanographenes **9**–**12**. **9** and **10** contain the same numbers of π -electrons (60) as **4**, while **11** contain a larger number of π -electrons (96).¹¹ Yet, the optical band gap for **4** is smaller than for **9** (≈ 2.40 eV), **10** (≈ 2.19 eV), and **11** (≈ 1.98 eV). The optical characteristics of **4** are found to be strikingly similar

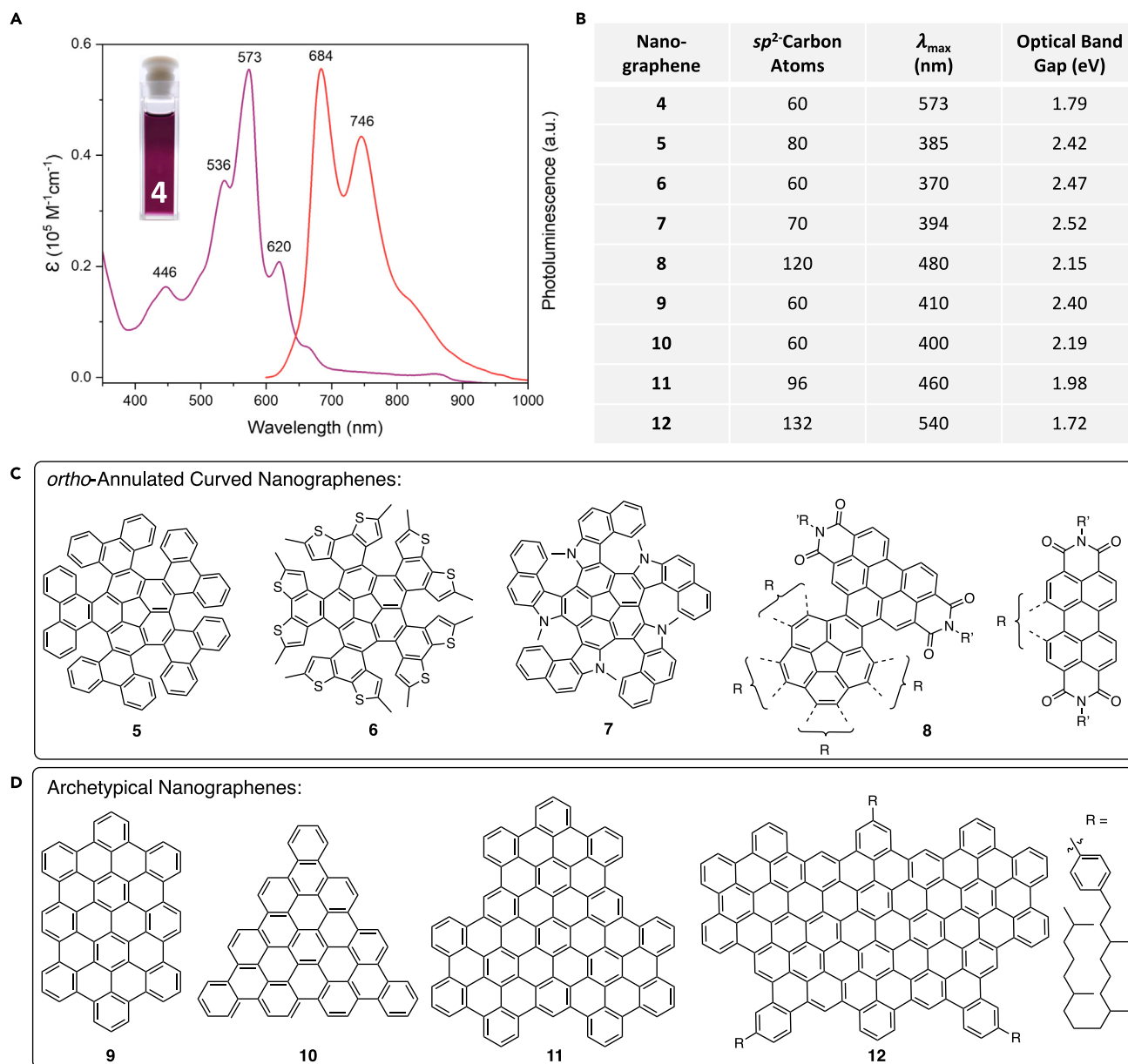


Figure 7. Optical properties comparison

(A) UV-vis absorption (purple line) and fluorescence (red line) spectra of **4** in chlorobenzene at a concentration of 4.23×10^{-6} mol/L along with the digital picture of the solution. Fluorescence spectrum was acquired upon excitation at 400 nm.

(B) Properties of nanographenes **4–12**.

(C) Chemical structures of *ortho*-annulated nanographenes.

(D) Chemical structures of archetypical nanographenes.

to an atomically precise graphene quantum dot **12**, which is composed of 2.2 times larger sp^2 -carbon atom footprint.⁵¹ While the absorption range is similar, the bands are red shifted in **4**. Interestingly, three long alkyl chains ($C_{20}H_{41}$) are required for the solubilization of **12**. Yet, in comparison with **4**, the vibronic features appear broad, indicating ill-defined aggregation and limited solubility. Overall, this indicates superior electronic properties of **4** over *ortho*-annulated and planar nanographene structures.

The electrochemical behavior of **4** was examined by square-wave voltammetry (SWV) and cyclic voltammetry (CV) experiments (Figure S46; Table S16). These results indicated electron-deficient nature of **4** akin to other curved aromatics such as corannulene (which accepts up to 4 electrons) and fullerene C₆₀ (which accepts up to 6 electrons). In total, five quasi-reversible reductions were observed for **4**. The first one-electron reduction occurred at −1.75 V versus the ferrocene/ferrocenium couple (Fc/Fc⁺). This indicated that 5-fold *peri*-annulations led to a higher electron affinity (with an anodic shift of 0.74 V for the first reduction) than the nanographene core.⁵² Finally, the frontier molecular orbital (highest occupied molecular orbital [HOMO] and lowest unoccupied molecular orbital [LUMO]) energies were calculated at the ωB97X-D/Def2TZVPP level (Figure 6D). The HOMO is mainly delocalized through the *peri*-annulated region. By contrast, the LUMO spans across the nanographene core. This is suggestive of a D-π-A character of the overall molecule and likely to be the cause of the observed red shift and the low band gap.⁵³

Conclusions

In summary, 5-fold *peri*-annulations on a corannulene core lead to the formation of a bowl-helix hybrid chiral nanographene structure. It exhibits absorption in the 400–850 nm range and fluorescence emission in the 650–900 nm range. In solvents of low dielectric constants, such as chloroform, benzene, and toluene, the nanographene exists as a dimer, which shows stability at millimolar concentrations and temperatures of up to 50°C. The equilibrium can be shifted to monomer in solvents of high dielectric constants, such as chlorobenzene, 1,2-dichlorobenzene, and nitrobenzene, or upon dilution to micromolar concentrations. In the solid state, two pairs of C₅-symmetric enantiomers pack in 2D arrays by adopting concave-concave and convex-convex packing arrangements. A soft ionization technique, HR-APCI-MS, demonstrated the stability of the supramolecular nanographene bilayer in the gas phase. Theoretical calculations indicated dimerization to be unfavorable for the pristine core molecule. Whereas bilayer formation was found to be spontaneous and stabilized mainly by aromatic interactions and aided by dispersion forces in the nanographene structure. Introduction of fullerene C₆₀ leads to the formation of host-guest complexes. The fullerene guest is nested in the bilayer nanographene hosts through shape complementarity and π-π stacking interactions. This complex presents a five-layered structure comprising of 300 sp²-carbon atoms arranged in a 2 × 1.5 nm space. Similar bowl-helix hybrid structures obtained upon *ortho*-annulations neither exhibit long wavelength optical properties nor any tendency to self-assemble into supramolecular structures. A comparison with archetypical nanographenes also indicates a significantly low optical band gap of the present structure. Thus, the work presented here underlines the importance of *peri*-annulations in the synthesis of nanographenes with superior electronic and self-assembling properties. Furthermore, since chiral compounds are known to affect the spins of the electrons passing through them, a phenomenon known as the chiral-induced spin-selectivity effect,⁵⁴ the present molecular design, and its possible higher chalcogen variants (selenium and tellurium analogs) may provide interesting bilayer materials for the field of spintronics.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Mihaela C. Stuparu (mstuparu@ntu.edu.sg).

Materials availability

All materials generated in this study are available from the [lead contact](#) without restriction.

Data and code availability

The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC 2322072 (compound **4**) and CCDC 2322073 (**4** = **C₆₀**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.chempr.2024.07.008>.

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AUTHOR CONTRIBUTIONS

Z.Z. carried out all the experimental work and prepared data figures. M.C.S. conceived the project and supervised it. D.C. carried out the computational studies relating to monomer conformation, dimerization aspects, and frontier molecular orbitals and described them. D.C., Z.Z., and M.C.S. discussed the association constant studies. I.F. carried out the computational studies related to the NCI plot. M.C.S. prepared the manuscript and revised it with the help of D.C. and Z.Z.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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