Synthesis and Properties of Bis-corannulenes

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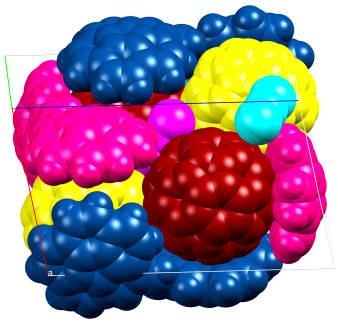
Supporting Information Placeholder



ABSTRACT: Corannulenecarbaldehyde and corannulenylmethyl triphenylphosphonium bromide are combined through the Wittig olefination reaction to furnish dicorannulenylethene with 70% yield. A subsequent oxidative photocyclization leads to annulation of the corannulene nuclei to produce a $C_{42}H_{18}$ nanographene structure in 59% yield. Interestingly, only the *trans* isomer of the dicorannulenylethene forms co-crystals with fullerene C_{60} through concave-convex and convex-convex π-π stacking interactions. The Mallory photocyclization could be extended to a phenanthrene-based diarylethene precursor to yield a large bi-corannulene system.

Corannulene is a fascinating molecular motif in the chemistry of polycyclic aromatic hydrocarbons.[1-3] Lawton and Barth envisioned it in 1966 and developed the first synthesis which involved 17 steps with an overall yield of 0.4%.[4] Quarter of a century later, Scott's flash vacuum pyrolysis reduced the synthetic efforts to five steps.[5] Further optimizations led to a highly efficient gas-phase synthesis which required only three steps and provided an overall isolated yield of 26%.[6] Siegel's synthesis brought with it the advantages of the solution-phase chemistry.[7] Sygula and Rabideu's discovery that curvature-forming step could simply be carried out under aqueous basic conditions made the synthesis highly practical.[8] These synthetic developments granted access to the molecule and exploration of its properties. These studies established that corannulene could accept electrons,[9] participate in host-guest interactions,[10] and display a bowl-to-bowl inversion process.[11-12] Due to these properties, corannulene has emerged as a unique building block in the design of functional materials.[13-16] In this regard, a particularly appealing direction is to harness its curvature in the preparation of non-planar nanographene structures.[17] Scott demonstrated feasibility of this concept by synthesizing a short carbon nanotube.[18] Later Scott and Itami established the synthesis of a warped carbon sheet.[19] Recently, Würthner showed synthesis of a large molecular bowl of carbon.[20] In these designs, corannulene acts as a bent core and planar aromatic fragments are welded to it in a radial fashion to expand the curved molecular structure. An alternative approach is to increase the number of corannulenes in the system. This latter concept to non-planar nanographenes is observed in Sygula's elegant dimeric[21-22] and trimeric[23-24] systems constructed by the Diels-Alder chemistry.[25-26] Significance of combining multiple corannulenes in one structure can also be seen from the work of Álvarez and coworkers in designing hosts of fullerene C_{60}.[27-32] Finally, works by Scott, Shenhar, and Petrukhina indicate interesting possibilities of bis-corannulenes in forming metal complexes.[33-37] Inspired by these studies, we envisaged that the photochemical synthesis, commonly referred to as a Mallory reaction,[38] might allow for two corannulenes to be annulated into a twin structure (Scheme 1). Such a molecule has the potential for further fusion into a longitudinal nanographene stripe (Figure 1). Similar to phenanthrene reactivity, the bridge C=C positions may also be available for functionalization in such nanostructures.

To probe feasibility of the aforementioned concept, corannulene was converted into carbaldehyde **1** through a Rieche formylation reaction (Scheme 1).[39] The carbaldehyde **1** could be reduced, brominated, and transformed into the corannulenylmethyl triphenylphosphonium bromide salt **2**.[40-41] The Wittig reaction[42] between **1** and **2** generates dicorannulenylethene **3**. A subsequent photochemically-induced oxidative cyclization process then enables the annulation of the corannulene nuclei to create structure **4**. The dicorannulenylethene formation and the photochemical annulation processes proceed with the isolated yields of 70 and 59%, respectively.

Scheme 1. Synthesis of bis-corannulenes **3** and **4**.

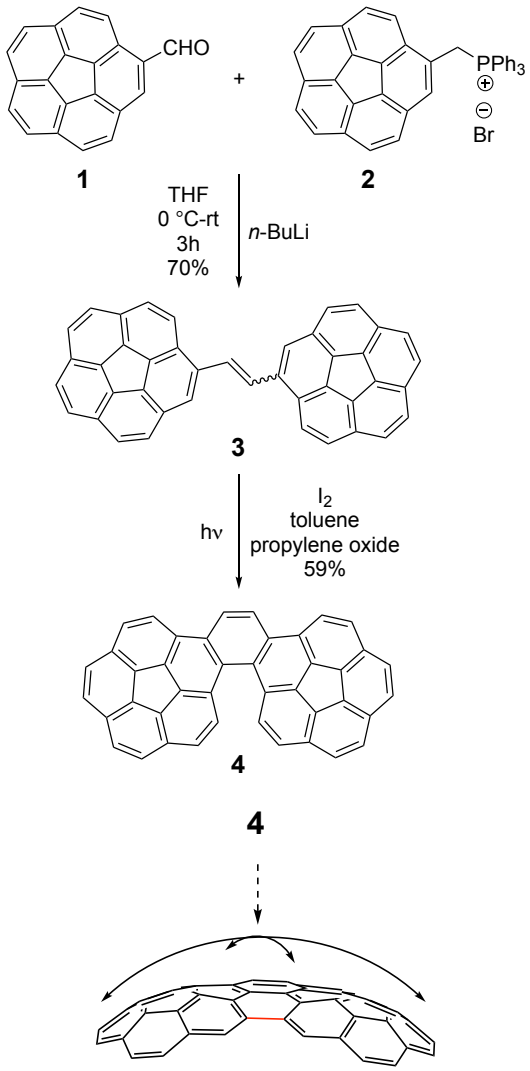


Figure 1. Hypothetical long and shallow molecular bowl that can potentially be accessed from **4**.

Compound **4** exhibited significantly lower solubility in common organic solvents as compared to **3**. However, the solubilities were sufficient for analyzing the compounds by ^{1}H NMR spectroscopy (See Supporting Information). The ^{1}H-NMR spectrum of compound **3** appeared complex due to a mixture of *cis* and *trans* isomer products upon the Wittig reaction. Upon oxidative photocyclization, however, the ^{1}H-NMR simplified as both the isomers lead to the formation of only one symmetric structure (**4**). A significant downfield shift for all the signals suggested the formation of an extended aromatic structure. MALDI-TOF mass analysis revealed the parent ion peaks at m/z = 524.1559 (calculated for $C_{42}H_{20}[M]^+$ = 524.1565) and at m/z = 522.1411 (calculated for $C_{42}H_{18}[M]^+$ = 522.1409) for compounds **3** and **4**, respectively (Figure S1-S2). In UV/Vis absorption spectra, a bathochromic shift was observed for compounds **3** and **4** when compared to pristine corannulene (Figure S3-S5). The fluorescence spectra showed emission bands in the range of 400-600 nm (Figure S6-S8). These photophysical properties indicated that the corannulenes were electronically coupled through conjugation of the delocalized electrons.

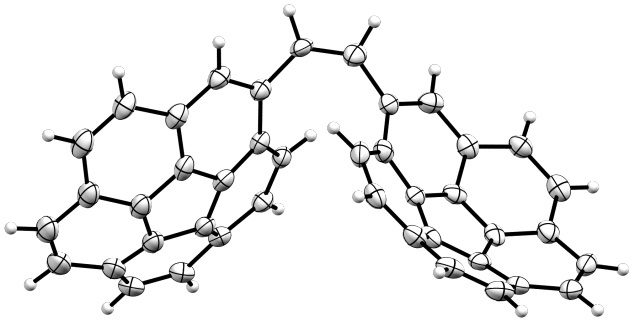


Figure 2. ORTEP representation of a crystal structure of *cis*-**3** with 50% probability of ellipsoids.

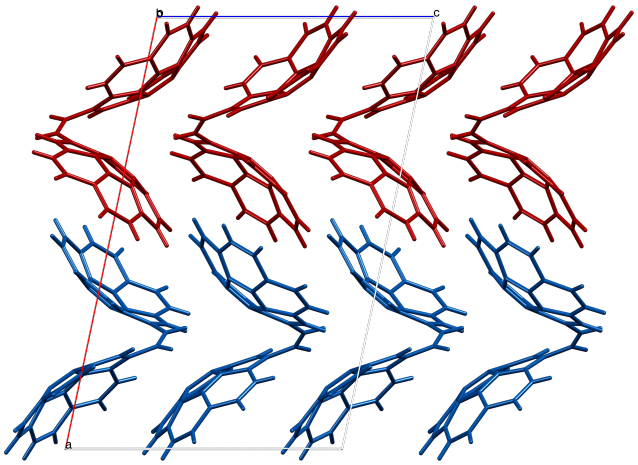


Figure 3. Molecular packing in a crystal structure of *cis*-**3**.

Having efficient access to the compounds, we focused on crystallization attempts in the absence and presence of fullerene C_{60}. These efforts led to the formation of only two types of X-ray quality single crystals.[43] A slow diffusion of hexane into dichloromethane led to the formation of yellow plate-like crystals belonging to the monoclinic P 1 21/c 1 space group from the *cis* isomer of **3**. The second type were black block-shaped co-crystals of the *trans* isomer of **3** and fullerene C_{60} formed upon slow evaporation of carbon disulfide and belonging to the triclinic P-1 space group. The bowl-depth of the corannulenes, defined as the mean distances between the central five-membered ring and the mean plane of the rim carbon atoms, are within the range of 0.84-0.88 Å in *cis*- and *trans*-**3** and similar to pristine corannulene (0.87 Å). The crystal structure of *cis*-**3** (Figure 2) consists of a layered arrangement of molecules in which the neighboring layers alternate with respect to the curvature of the corannulene nucleus (Figure 3). Bifurcated (2.6 and 2.7 Å) and single (2.8 Å) CH-π interactions dominate within the same layer while π-π interactions (3.3 Å) dominate within neighboring layers (Figure S9). In the co-crystals, the unit-cell consists of 4 molecules of fullerene C_{60} surrounded by 4 molecules of *trans*-**3** while 4 ordered solvent (CS_2) molecules occupy the remaining cell space (Figure 4 and Figure S10). In this arrangement, each fullerene C_{60} makes several concave-convex π-π stacking interactions (3.2-3.3 Å) with two corannulenes belonging to the two different *trans*-**3** molecules (Figure S11). It appears as though the *trans*-**3** molecules create walls of a box filled with precisely arranged four molecules each of fullerenes C_{60} and CS_2. These boxes are in turn held together by bifurcated π-π stacking interactions (3.1-3.3 Å)

between fullerenes and convex faces of the neighboring corannulene molecules.

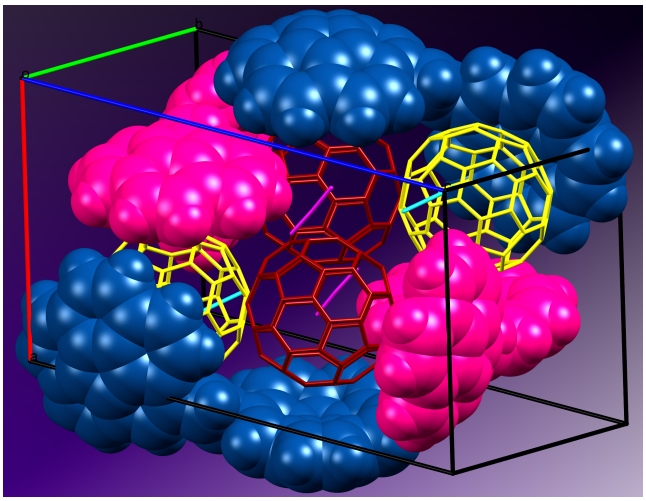
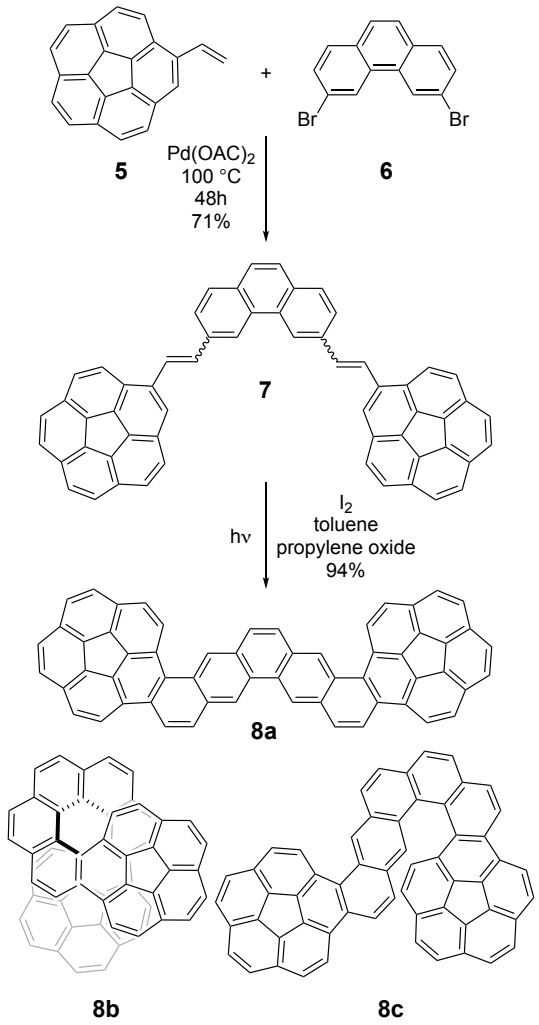


Figure 4. Molecular packing in a unit cell of a co-crystal of *trans*-**3** and fullerene C_{60}. The color-coding reflects symmetry equivalence in the crystal structure.

The versatility of Mallory cyclizations, in part, originates from different synthetic methods that can lead to the formation of the diarylethene precursors. For example, besides Wittig olefination, Heck reaction and olefin metathesis can both give practical access to stilbene-like precursors. In this regard, vinyl corannulene **5** can be prepared from corannulenecarbaldehyde in 78% isolated yield.[39] The palladium-catalyzed Heck reaction with 3,6-dibromophenanthrene (**6**)[44] then gives rise to precursor **7** in 71% yield (Scheme 2) (Figure S12-S14). The oxidative photocyclization reaction, in theory, can form three possible structural isomers. Isomers **8a** and **8b** posses a plane of symmetry and are expected to give a simple pattern in the ^{1}H-NMR spectrum. Furthermore, two singlets with a 2:1 area integration ratio are expected from the central phenanthrene motif in **8a**. The isomer **8b**, on the other hand, would present only one singlet from the central aromatic ring. It is only in the case of **8c** that two singlets are expected in a 1:1 ratio. The ^{1}H-NMR spectrum of the product displays two singlets at 9.5 and 10.1 ppm in a 1:1 ratio (see Supporting Information). Based upon these observations, it is reasonable to assume that photocyclization of **7** leads to formation of **8c** as the major isomer (yield = 94%) (Figure S15-S17).

In conclusion, dicorannulenylethene can be accessed with ease through Wittig reaction of corannulenecarbaldehyde and corannulenylmethyl triphenylphosphonium bromide. An oxidative photocyclization of this compound leads to the formation of a relatively large ($C_{42}H_{18}$) and curved π-system in good yield. Interestingly, only the *trans* isomer of dicorannulenylethene forms co-crystals with fullerene C_{60}. The crystalline arrangement can be visualized as a repeating arrangement of molecular boxes where each box is enclosed with 4 molecules of dicorannulenylethene and contains 4 molecules of fullerene C_{60}. The Heck reaction provides an alternative to the Wittig reaction and allows for insertion of a large fused ring system in-between the two corannulenes. We are now exploring the electrophilic halogenation of the bridge C=C bond in **4** as a potential route to introduce solubilizing groups and self-assembling synthons in the molecular structure. Such modifications will allow further investigations into the covalent (e.g., Scholl reaction for complete fusion of the molecular structure) and non-covalent (e.g., metal organic frameworks) chemistries of the presented new structural motif.

Scheme 2. Synthesis of bis-corannulenes **7** and **8**.



ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Synthesis and characterization details (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interests.

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REFERENCES

(1) Tsefrikas, V. M.; Scott, L. T. Geodesic polyarenes by flash vacuum pyrolysis. *Chem. Rev.* **2006**, *106* (12), 4868.

(2) Wu, Y.-T.; Siegel, J. S. Aromatic molecular-bowl hydrocarbons: synthetic derivatives, their structures, and physical properties. *Chem. Rev.* **2006**, *106* (12), 4843.

(3) Sygula, A. Chemistry on a Half-Shell: Synthesis and Derivatization of Buckybowls. *Eur. J. Org. Chem.* **2011**, 9, 1611.

(4) Barth, W. E.; Lawton, R. G. Dibenzo [ghi, mno] fluoranthene. *J. Am. Chem. Soc.* **1966**, *88* (2), 380.

(5) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. Corannulene. A convenient new synthesis. *J. Am. Chem. Soc.* **1991**, *113* (18), 7082.

(6) Scott, L. T.; Cheng, P. C.; Hashemi, M. M.; Bratcher, M. S.; Meyer, D. T.; Warren, H. B. Corannulene. A Three-Step Synthesis. *J. Am. Chem. Soc.* **1997**, *119* (45), 10963.

(7) Seiders, T. J.; Baldridge, K. K.; Siegel, J. S. Synthesis and Characterization of the First Corannulene Cyclophane. *J. Am. Chem. Soc.* **1996**, *118* (11), 2754.

(8) Sygula, A.; Rabideau, P. W. A Practical, Large Scale Synthesis of the Corannulene System. *J. Am. Chem. Soc.* **2000**, *122* (26), 6323.

(9) Ayalon, A.; Rabinovitz, M.; Cheng, P.C.; Scott, L. T. Corannulene tetraanion: a novel species with concentric anionic rings. *Angew. Chem. Int. Ed.* **1992**, *31* (12), 1636.

(10) Sygula, A. Corannulene-Adorned Molecular Receptors for Fullerenes Utilizing the π–π Stacking of Curved-Surface Conjugated Carbon Networks. Design, Synthesis and Testing. *Synlett* **2016**, *27* (14), 2070.

(11) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. Corannulene Bowl-to-Bowl Inversion Is Rapid at Room-Temperature. *J. Am. Chem. Soc.* **1992**, *114* (5), 1920.

(12) Seiders, T. J.; Baldridge, K. K.; Grube, G. H.; Siegel, J. S. Structure/Energy Correlation of Bowl Depth and Inversion Barrier in Corannulene Derivatives: Combined Experimental and Quantum Mechanical Analysis. *J. Am. Chem. Soc.* **2001**, *123* (4), 517.

(13) Rice, A. M.; Dolgopolova, E. A.; Shustova, N. B. Fulleretic Materials: Buckyball- and Buckybowl-Based Crystalline Frameworks. *Chem. Mater.* **2017**, *29* (17), 7054.

(14) Zabula, A. V.; Spisak, S. N.; Filatov, A. S.; Rogachev, A. Y.; Petrukhina, M. A. Record Alkali Metal Intercalation by Highly Charged Corannulene. *Acc. Chem. Res.* **2018**, *51* (6), 1541.

(15) Nestoros, E.; Stuparu, M. C. Corannulene: a molecular bowl of carbon with multifaceted properties and diverse applications. *Chem. Commun.* **2018**, *54* (50), 6503.

(16) Saito, M.; Shinokubo, H.; Sakurai, H. Figuration of bowl-shaped π-conjugated molecules: properties and functions. *Mater. Chem. Front.* **2018**, *2* (4), 635.

(17) Muzammil, E. M.; Halilovic, D.; Stuparu, M. C. Synthesis of corannulene-based nanographenes. *Commun. Chem.* **2019**, *2* (1), 58.

(18) Scott, L. T.; Jackson, E. A.; Zhang, Q.; Steinberg, B. D.; Bancu, M.; Li, B. A Short, Rigid, Structurally Pure Carbon Nanotube by Stepwise Chemical Synthesis. *J. Am. Chem. Soc.* **2012**, *134* (1), 107.

(19) Kawasumi, K.; Zhang, Q.; Segawa, Y.; Scott, L. T.; Itami, K. A grossly warped nanographene and the consequences of multiple odd-membered-ring defects. *Nat. Chem.* **2013**, *5* (9), 739.

(20) Shoyama, K.; Würthner, F. Synthesis of a Carbon Nanocone by Cascade Annulation. *J. Am. Chem. Soc.* **2019**, *141* (33), 13008.

(21) Sygula, A.; Fronczek, F. R.; Sygula, R.; Rabideau, P. W.; Olmstead, M. M. A Double Concave Hydrocarbon Buckycatcher. *J. Am. Chem. Soc.* **2007**, *129* (13), 3842.

(22) Kumarasinghe, K. G. U. R.; Fronczek, F. R.; Valle, H. U.; Sygula, A. Bis-corannulenoanthracene: An Angularly Fused Pentacene as a Precursor for Barrelene-Tethered Receptors for Fullerenes. *Org. Lett.* **2016**, *18* (13), 3054.

(23) Yanney, M.; Fronczek, F. R.; Henry, W. P.; Beard, D. J.; Sygula, A. Cyclotrimerization of Corannulyne: Steric Hindrance Tunes the Inversion Barriers of Corannulene Bowls. *Eur. J. Org. Chem.* **2011**, *2011* (33), 6636.

(24) Yanney, M.; Fronczek, F. R.; Sygula, A. Corannulene Subunit Acts as a Diene in a Cycloaddition Reaction: Synthesis of $C_{80}H_{32}$ Corannulyne Tetramer. *Org. Lett.* **2012**, *14* (18), 4942.

(25) Sygula, A.; Sygula, R.; Rabideau, P. W. The First Buckybowl Aryne. Corannulyne: A Nonplanar Benzyne. *Org. Lett.* **2005**, *7* (22), 4999.

(26) Sygula, A.; Sygula, R.; Rabideau, P. W. Isocorannulenofuran: A Versatile Building Block for the Synthesis of Large Buckybowls. *Org. Lett.* **2006**, *8* (25), 5909.

(27) Álvarez, C. M.; García-Escudero, L. A.; García-Rodríguez, R.; Martín-Álvarez, J. M.; Miguel, D.; Rayón, V. M. Enhanced association for C_{70} over C_{60} with a metal complex with corannulene derivate ligands. *Dalton Trans.* **2014**, *43* (42), 15693.

(28) Álvarez, C. M.; Aullón, G.; Barbero, H.; García-Escudero, L. A.; Martínez-Pérez, C.; Martín-Álvarez, J. M.; Miguel, D. Assembling Nonplanar Polyaromatic Units by Click Chemistry. Study of Multicorannulene Systems as Host for Fullerenes. *Org. Lett.* **2015**, *17* (11), 2578.

(29) Álvarez, C. M.; Barbero, H.; Ferrero, S.; Miguel, D. Synergistic Effect of Tetraaryl Porphyrins Containing Corannulene and Other Polycyclic Aromatic Fragments as Hosts for Fullerenes. Impact of C_{60} in a Statistically Distributed Mixture of Atropisomers. *J. Org. Chem.* **2016**, *81* (14), 6081.

(30) Barbero, H.; Ferrero, S.; Álvarez-Miguel, L.; Gómez-Iglesias, P.; Miguel, D.; Álvarez, C. M. Affinity modulation of photoresponsive hosts for fullerenes: light-gated corannulene tweezers. *Chem. Commun.* **2016**, *52* (88), 12964.

(31) García-Calvo, V.; Cuevas, J. V.; Barbero, H.; Ferrero, S.; Álvarez, C. M.; González, J. A.; Díaz de Greñu, B.; García-Calvo, J.; Torroba, T. Synthesis of a Tetracorannulene-perylenediimide That Acts as a Selective Receptor for C_{60} over C_{70}. *Org. Lett.* **2019**, *21* (15), 5803.

(32) Ferrero, S.; Barbero, H.; Miguel, D.; García-Rodríguez, R.; Álvarez, C. M. Octapodal Corannulene Porphyrin-Based Assemblies: Allosteric Behavior in Fullerene Hosting. *J. Org. Chem.* **2020**, *85* (7), 4918.

(33) Eisenberg, D.; Filatov, A. S.; Jackson, E. A.; Rabinovitz, M.; Petrukhina, M. A.; Scott, L. T.; Shenhar, R. Bicorannulenyl: Stereochemistry of a $C_{40}H_{18}$ Biaryl Composed of Two Chiral Bowls. *J. Org. Chem.* **2008**, *73* (16), 6073.

(34) Zabula, A. V.; Sevryugina, Y. V.; Spisak, S. N.; Kobryn, L.; Sygula, R.; Sygula, A.; Petrukhina, M. A. An unsolvated buckycatcher and its first dianion. *Chem. Commun.* **2014**, *50* (20), 2657.

(35) Eisenberg, D.; Jackson, E. A.; Quimby, J. M.; Scott, L. T.; Shenhar, R. The Bicorannulenyl Dianion: A Charged Overcrowded Ethylene. *Angew. Chem. Int. Ed.* **2010**, *49* (41), 7538.

(36) Eisenberg, D.; Quimby, J. M.; Jackson, E. A.; Scott, L. T.; Shenhar, R. Highly charged supramolecular oligomers based on the dimerization of corannulene tetraanion. *Chem. Commun.* **2010**, *46* (47), 9010.

(37) Sumner, N. J.; Spisak, S. N.; Filatov, A. S.; Rogachev, A. Y.; Zabula, A. V.; Petrukhina, M. A. Double-Concave Binding of Bicorannulenyl Dianion: Cesium vs Lithium Salts. *Organometallics* **2014**, *33* (11), 2874.

(38) Mallory, F. B.; Mallory, C. W. *Photocyclization of Stilbenes and Related Molecules*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 1984; pp 1–456.

(39) Rajeshkumar, V.; Lee, Y. T.; Stuparu, M. C. Corannulenecarbaldehyde: High-Yielding Synthesis by Rieche Formylation and Facile Access to a Variety of Corannulene Derivatives. *Eur. J. Org. Chem.* **2016**, *2016*, 36.

(40) Rajeshkumar, V.; Stuparu, M. C. A photochemical approach to aromatic extension of the corannulene nucleus. *Chem. Commun.* **2016**, *52*, 9957.

(41) Halilovic, D.; Budanović, M.; Wong, Z. R.; Webster, R. D.; Huh, J.; Stuparu, M. C. Photochemical Synthesis and Electronic Properties of Extended Corannulenes with Variable Fluorination Pattern. *J. Org. Chem.* **2018**, *83* (7), 3529.

(42) Wittig, G.; Geissler, G. Zur Reaktionsweise des Pentaphenylphosphors und einiger Derivate. *Justus Liebigs Annalen der Chemie* **1953**, *580* (1), 44.

(43) CCDC 2047888 and CCDC 2047889 contains the crystallographic data. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

(44) Junseok, S.; So-Ra, P.; Mina, K.; Chul, S. M.; Jihoon, L. The role of electron-transporting Benzo[f]quinoline unit as an electron acceptor of new bipolar hosts for green PHOLEDs, *Dyes and Pigments*, **2019**, *162*, 959-966.