π-Conjugated Discrete Oligomers Containing Planar and Nonplanar Aromatic Motifs

Ji Li,[†,#] Anamaria Terec,[∥,#] Yue Wang,[‡] Hrishikesh Joshi,[†] Yunpeng Lu,[†] Handong Sun,[‡,§] and Mihaiela C. Stuparu*[,†,⊥]

[†]Division of Chemistry and Biological Chemistry, [‡]Division of Physics and Applied Physics, [§]Centre for Disruptive Photonic Technologies, School of Physical and Mathematical Sciences, Nanyang Technological University, 21-Nanyang Link, 637371, Singapore

[∥]Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, 11 Arany Janos, Cluj-Napoca 400028, Romania

[⊥]School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

S *Supporting Information*

ABSTRACT: A new family of π-conjugated oligomers featuring a nonplanar polycyclic aromatic hydrocarbon, corannulene, and a planar aromatic unit, thiophene, is synthesized through an iterative metal-catalyzed coupling protocol. The two structural motifs are connected through an acetylene linkage. In the shorter oligomers, a thiophene unit is attached to one or two corannulenes. In the higher analogues, two, three, and four thiophene units are placed in an alternating fashion with three, four, and five corannulene units, respectively. Photophysical studies reveal extended π-effects that initially increase and then attenuate as a function of the oligomer length. Notably, longer oligomers are found to be

highly active for nonlinear absorption and emission properties. The oligomer with three corannulene and two thiophene units exhibits a two-photon absorption cross section of 600 GM and two-photon-excited intense green luminescence. This work, therefore, introduces the concept of combining planar and nonplanar aromatic motifs in the design of π-conjugated discrete oligomers, establishes synthetic feasibility of such hybrid materials, reports on their photophysical properties that is anticipated to have significant implications for future research targets, and features the discovery that corannulene derivatives can exhibit excellent nonlinear optical activity when extended through π-bridges.
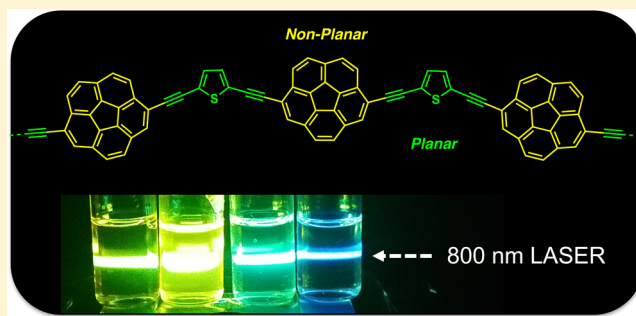
■ INTRODUCTION

Discrete π-conjugated oligomers have been the focus of intense research investigations in recent years.[1−18] This is primarily due to their many applications in the arena of organic electronics. So far, however, the emphasis is placed mainly on planar aromatic components for the construction of such high molecular weight yet monodisperse entities. Studies in which nonplanar building blocks are included into the oligomer structure are rare.[19] To increase the repertoire of such hybrid structures, we envisaged that corannulene, a bowl-shaped aromatic hydrocarbon, can be introduced into the molecular design (Figure 1). This nonplanar motif is a remarkable polycyclic structure that exhibits many interesting properties.[20−22] For instance, corannulene can accept electrons.[23,24] It can undergo a bowl-inversion process.[25−28] It can stack to yield liquid crystalline phases that can respond to electrical stimulus.[29] It can recognize fullerene C_{60} through ball-and-socket type of π−π stacking interactions.[30−33] Hence, buckyball composites can be prepared through inclusion of the corannulene motif into a polymer structure.[34,35] Remarkably, phenylene ethynylene derivatives of corannulene are shown to
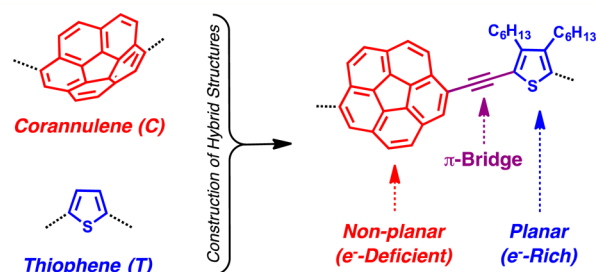

Figure 1. Chemical structures of the planar and nonplanar structural motifs employed in this study to prepare π-conjugated discrete oligomers.

give rise to blue light emitting diodes.[36] Furthermore, extended corannulene systems are established to be good active components in field-effect transistors.[37,38] Last but not least, metal organic frameworks with redox activity have been prepared using corannulene derivatives.[39] Thus, far, however,

discrete oligomers of corannulene, varying in the length of the molecular structure and number of corannulene units, have not been reported.[40] Synthetic access to such materials will help us understand the properties of such unique structures as a function of their molecular length. These oligomers will also serve as model compounds for the analogous polymer structure. Furthermore, prospects of preparing supramolecular complexes with C_{60} appear enticing. In this context, here, we discuss: (i) the notion of combining the planar and nonplanar structures in the design of π-conjugated discrete materials, (ii) development of a synthetic strategy that can give access to such oligomers, (iii) a detailed photophysical study revealing the rise and attenuation of electronic communication between the two structural motifs as a function of overall molecular length and its implication on future research targets especially with respect to polymeric analogues, and (iv) the discovery that structures based on corannulene are capable of exhibiting excellent two-photon absorption and emission activities.

■ RESULTS AND DISCUSSION

In considering preparation of large molecular structures through stepwise synthetic protocols, three elements are important. First, the building blocks necessary should be available in an efficient manner and at a considerable scale. Next, an efficient reaction is required to couple the building blocks in order to construct the higher analogues in a practical fashion. Third, side-chains are crucial in the molecular design that endows solubility to the oligomers during the reaction and the purification processes.

Keeping this in mind, corannulene-based terminal alkyne derivatives can be easily accessed through their bromide precursors.[41−44] And palladium catalyzed Sonogashira−Hagihara coupling is a highly efficient protocol that allows for C−C bond formation between such corannulene alkynes and a variety of electronically active aromatic halides.[45] Therefore, we choose to employ corannulene-based acetylenes as one building block and the transition metal-catalyzed cross-coupling reaction as the oligomer growth process. As for the second building block, a thiophene diiodide unit is chosen. This is due to various properties of the thiophene nucleus. For instance, high polarizability of the sulfur atom in thiophene groups leads to a stabilization of the conjugated chain and to excellent charge transport properties.[46−48] This is one of the reasons that thiophene derivatives have found many applications in organic and molecular electronics. Finally, long alkyl side chains are placed on the thiophene nucleus for enhancing the solubility of the materials.

After envisioning the molecular design, the simplest structure C_1T_1 (Scheme 1) was targeted. In this structure, a corannulene unit is attached to a thiophene unit through an acetylene linkage. The synthesis began with bromocorannulene, which was accessed through bromination of bare corannulene.[49] A Sonogashira-Hagihara coupling reaction between bromocorannulene and trimethylsilyl (TMS) acetylene allowed for installation of the alkyne unit onto the corannulene scaffold.[41−43] Subsequent removal of the TMS group through use of potassium carbonate in methanol gave rise to terminal acetylene 1. On the other hand, dihexyl substituted thiophene was iodinated to afford dihalide 2. A further palladium-catalyzed cross-coupling reaction between 1 and an excess of 2 furnished 3. Finally, deiodination of 3 resulted in formation of C_1T_1 in an isolated yield of 65%. The removal of iodine group was necessary to avoid its interference in the photophysical

**Scheme 1. Synthesis of the Shorter Oligomers**[a]
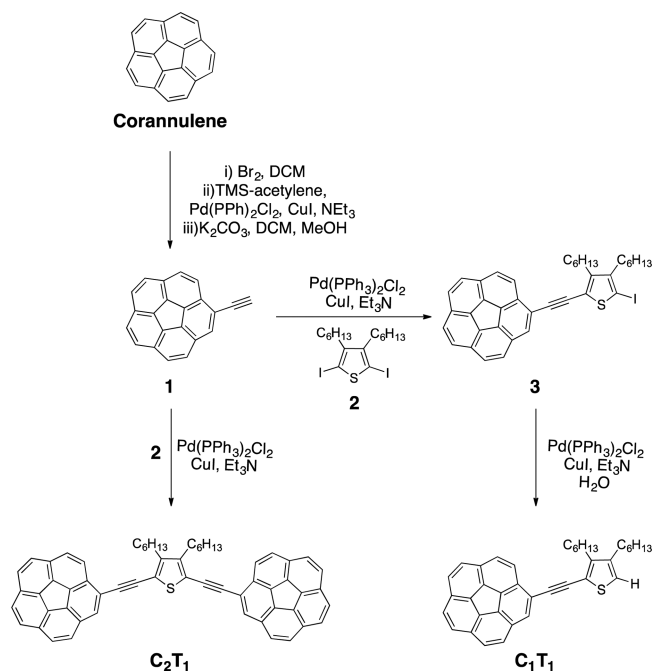
[a]For the acronyms, C stands for corannulene and T for thiophene, and the subscript indicates the number of repeating units.

properties of the molecule (also known as "heavy atom effect") and for establishing a proper comparison between the targeted oligomer series. After successful preparation of C_1T_1, oligomer C_2T_1 with a thiophene unit flanked by two corannulene units was accessed through the palladium catalyzed coupling reaction between 1 and 2 (Scheme 1). In this case, acetylene 1 was used in excess to afford bis-coupled product C_2T_1 in an isolated yield of 72%.

Encouraged by the synthesis of the first two target structures, further lengthening of the molecular structure was planned. For this, 1,6-dibromo-2,5-dimethyl-corannulene, 4, with two reactive sites for the oligomer growth process, was prepared.[49] The bromine atoms allowed for installation of TMS-protected acetylene units onto the corannulene scaffold through Sonogashira-Hagihara coupling reaction (Scheme 2).[42,49] Subsequent removal of the TMS groups furnished the free bis-acetylene molecule 5. Finally, a double cross-coupling reaction between terminal alkynes of 5 with aryl iodide 3 resulted in formation of oligomer C_3T_2 in 70% isolated yield.

To further increase the corannulene content, oligomers with longer length were targeted. To achieve this, a slightly complex synthetic route was adopted. In this route, a corannulene derivative carrying free acetylene and a protected acetylene was prepared. To accomplish this, bis-TMS protected compound (5-TMS) used previously in the synthesis of C_3T_2 was subjected to a protective group exchange with an acetonide group (Scheme 3). This was achieved through an in situ removal of the TMS groups and subsequent protection of the resulting free acetylenes with acetone molecules through use of potassium hydroxide. In this way, 1,6-diacetonide-2,5-dimethyl-corannulene 6 was accessed. Removal of the acetonide group provided a mixture of mono- and bis-protected acetylene compounds 7 and 5. Due to the polarity difference in the completely deprotected compound (5) and monoacetonide compound (7), column chromatography offered a simple way
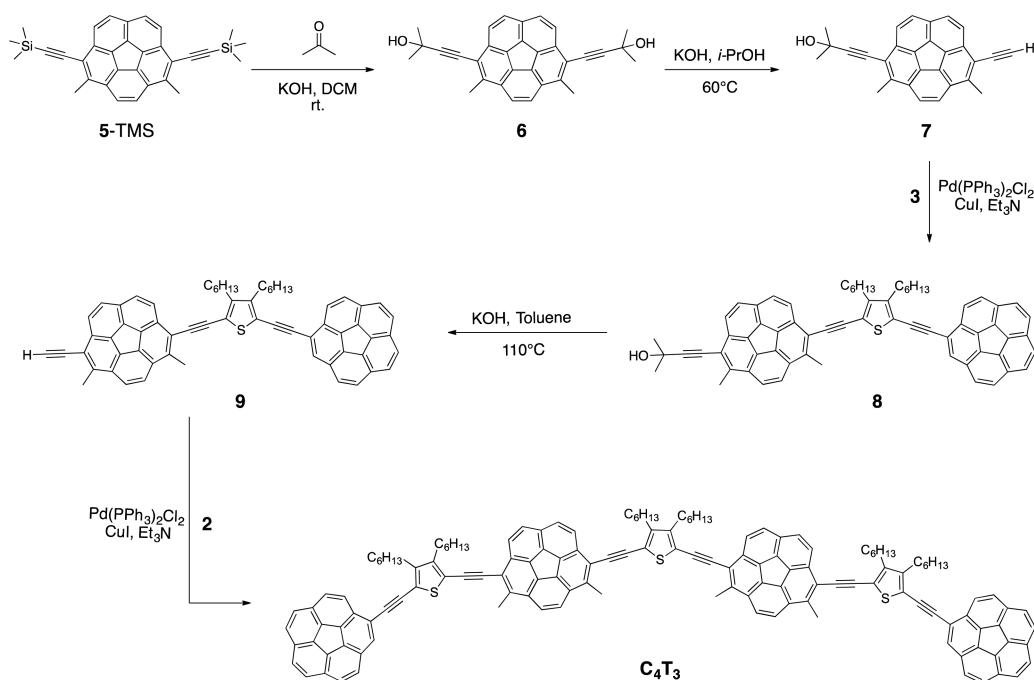
Scheme 2. Synthesis of C$_3$T$_2$
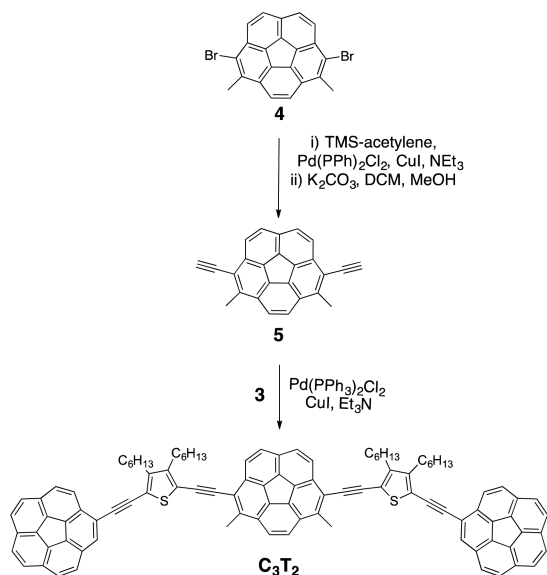
of separating the two compounds. This is not the case when bis-TMS-protected compound (**5-TMS**) is subjected directly to a protective group removal reaction, as the resulting mono- and bis-TMS protected compounds exhibit very little difference in their R_f values and therefore a very difficult separation. The isolated compound **7** could now be subjected to a palladium catalyzed coupling reaction with compound **3** to give monoacetonide compound **8**. Removal of the acetonide group in **8** using potassium hydroxide in toluene yielded free acetylene **9**. A subsequent coupling reaction of **9** with **2** finally affords oligomer **C$_4$T$_3$** carrying four corannulene and three thiophene units in an isolated yield of 27%.

Having compound **9** in hand, cross-coupling reaction with an excess of thiophene-diiodide **2** afforded compound **10** with a

terminal halide group (Scheme 4). A subsequent palladium-catalyzed coupling of this compound with corannulene bis-acetylene **5** yielded oligomer **C$_5$T$_4$** (23% isolated yield) carrying five corannulene units alternated with three thiophene ethynylene linkages. The synthesized compounds were characterized using NMR spectroscopy. In MALDI-TOF mass spectrometry, a clear isotopic pattern of the molecular ions for all the prepared oligomers could be seen (Figure 2). Unfortunately, the longest oligomer, **C$_5$T$_4$**, was found to have very little solubility in a large variety of solvents. Therefore, it was excluded from the subsequent properties study.

To study optical properties of the oligomers as a function of their length, initially, UV−vis absorption spectroscopy was employed. This study suggested that an increase in the molecular length resulted in a bathochromic shift in the absorption spectrum of the oligomers (Figure 3 and Table 1). The shift between the first two oligomers was significant (∼50 nm). To the third oligomer, however, it decreased drastically to about 10 nm. The last two oligomers, on the other hand, showed similar absorption spectrum. The experimental results are in agreement with a DFT calculations-based theoretical study that shows a decrease in the HOMO−LUMO gap with an increase in the length of the structure (Table 1 and Figures S1−S15). The theoretical study indicates that the effective conjugation length, in the present series of structures, is reached at **C$_4$T$_3$/C$_5$T$_4$** level, as the band gap remains constant in the last two oligomers. Furthermore, a comparison of the shape of the HOMO orbital surfaces in the last two oligomers shows virtually no difference (Table 1 and Figure 4). Unfortunately, the insolubility of **C$_5$T$_4$** did not allow for practically confirming the theoretical result related to the effective conjugation length. However, based on the trend of decreasing red shift from **C$_1$T$_1$** to **C$_4$T$_3$**, and very little difference between the properties of **C$_3$T$_2$** and **C$_4$T$_3$**, it is reasonable to assume that effective conjugation length is reached at the **C$_4$T$_3$** level.

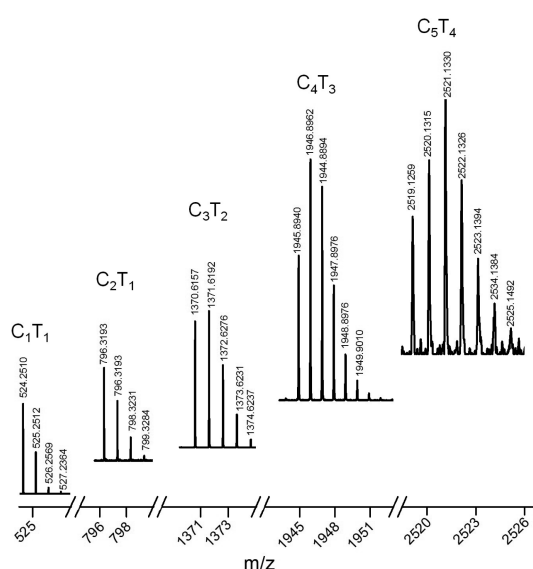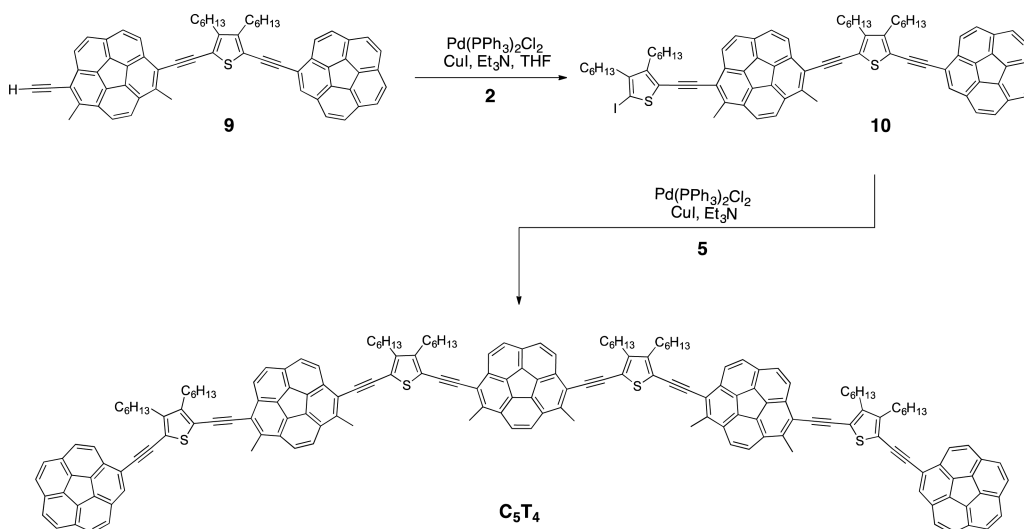**Scheme 3. Synthesis of C$_4$T$_3$**

Scheme 4. Synthesis of C₅T₄

Figure 2. MALDI-TOF mass spectra of the synthesized oligomer series.

At this point, it also became interesting to compare the properties of the current materials with known thiophene-based arylene ethynylene chromophores. In comparison to a molecule in which a thiophene nucleus is flanked by two phenylene acetylenes,[50] the absorption of all the oligomers (including that of the first one which contains only one acetylene bridge) was red-shifted. In comparison to a second and more vastly delocalized flat aromatic system in which two pyrene groups are attached to a thiophene through acetylene linkages,[51] the absorption of the first oligomer was blue-shifted, the second behaved in a similar fashion, and the third and fourth oligomers were red-shifted. These comparisons also helped in concluding that the corannulene nucleus was involved in the π-conjugation.

Next, fluorescence emission properties of the synthesized oligomer series were examined. This study suggested that the first oligomer (C₁T₁) exhibited a blue, second (C₂T₁) blue-green, and the next two oligomers (C₃T₂ and C₄T₃) a green emission (Figure 3). Once again, C₃T₂ and C₄T₃ behaved in a very similar fashion (in terms of emission wavelength and structure of the signal) confirming the aforementioned notion
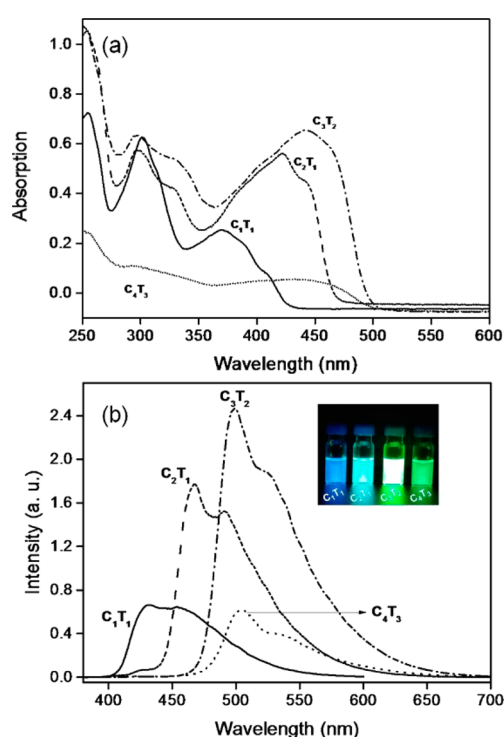

Figure 3. (a) UV/vis absorption spectra and (b) emission spectra of oligomers in CHCl₃ (4×10^{-4} M) excited at 370 nm.

Table 1. Summary of the Photophysical Properties of the Oligomers

sample	abs max (nm)	em max (nm)	Φf (%)	η (ns)	HOMO–LUMO (eV)[a]
C₁T₁	302, 370	430, 456	13.02	1.15	3.46
C₂T₁	298, 332, 422, 445	468, 491	36.04	1.3	2.87
C₃T₂	295, 332, 445, 465	498, 525	40.06	1.4	2.61
C₄T₃	450	505, 538	8.72	1.59	2.51
C₅T₄	insoluble				2.51

[a]Calculations were performed with Gaussian09. All structures were optimized with B3LYP/6-31G(d,p) method in the gas phase.
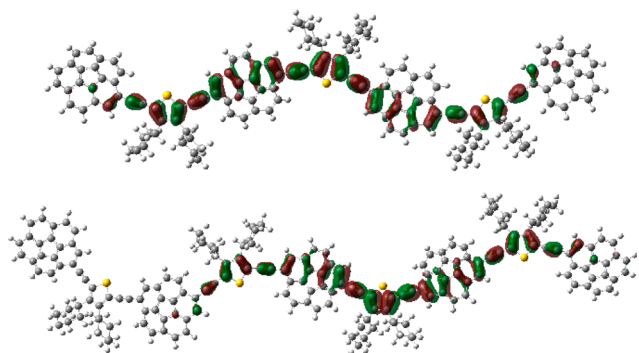
Figure 4. HOMO orbital surfaces for the last two oligomers, C_4T_3 (top) and C_5T_4 (bottom).

of properties saturation at this level. However, a significant difference between the two oligomers is the quantum yield of emission. On one hand, where C_3T_2 display a quantum yield of 40%, only 8% is observed for C_4T_3.

In general, the photophysical study suggests good electronic communication between the planar and nonplanar components through acetylene bridges. This interaction initially increases as a function of oligomer length (as seen in C_1T_1, C_2T_1, and C_3T_2) but then the π-conjugation effects tends to saturate (as seen in C_3T_2 and C_4T_3). Moreover, C_3T_2 seems to be an optimum structure in terms of solubility, longer wavelength absorption, and best quantum yield of emission in the series. In light of these, we believe that the future research in this direction must address the π-connectivity between the corannulene units to further modulate the electronic properties as the length of a "pentamer"/"heptamer" (C_3T_2/C_4T_3) (when each aromatic unit is considered as a repeating unit) seems satisfactory in attaining the effective conjugation length.

Having studied the linear absorption properties, we became interested in examining the nonlinear optical activity of the synthesized oligomer series (Figure 5). The motivation behind such an undertaking came from the fact that so far only the
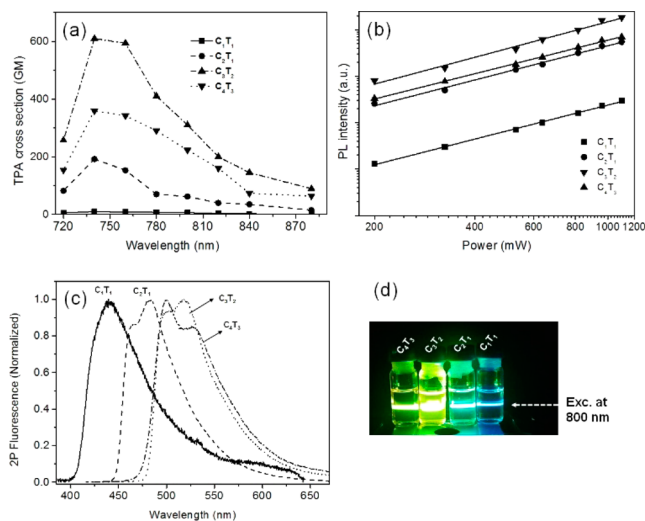

Figure 5. (a) Two-photon action spectra for C_1T_1, C_2T_1, C_3T_2, and C_4T_3 derivatives in CHCl$_3$. (b) Logarithmic plot of fluorescence output with excitation intensity of oligomers. (c) Two-photon excited emission of oligomers (4×10^{-4} M) in CHCl$_3$. (d) Photograph showing two-photon excited emission from oligomers excited at 800 nm femtosecond laser.

linear optical properties of a large variety of corannulene derivatives are studied in depth. The nonlinear optical characteristics remain largely unexplored. To this end, an 800 nm femtosecond laser with a pulse-width of 100 fs and a repetition rate of 1000 Hz was employed as the excitation source. The two-photon up-conversion process was evaluated by measuring input power intensity dependent changes upon excitation wavelength tuned from 720 to 900 nm. This wavelength range was chosen due to zero contribution of one-photon absorption from all the oligomers in this spectral region. The linear relation of emission intensities of the oligomers on the square of corresponding excitation power confirmed the two-photon process (Figure 5b). The two-photon absorption cross-section (2PA) was determined by means of two-photon excited fluorescence method as described by Xu and Webb.[52] This examination revealed that initially, as we go from C_1T_1 to C_2T_1 and C_3T_2, 2PA increased linearly with an increase in the oligomer length. However, the last oligomer exhibited a drop in the absorption cross-section. In this way, C_3T_2 with three corannulene and two thiophene units exhibited highest absorption cross section of 600 GM in the present oligomer series. Finally, two-photon excited fluorescence studies revealed blue to green emission for the shortest and the longer oligomers, respectively.

■ CONCLUSIONS

In essence, a careful design of the building blocks and coupling chemistry can give access to π-conjugated discrete oligomers with varying number of planar and nonplanar aromatic units. Corannulene, a bowl-shaped polycyclic aromatic hydrocarbon, is employed as the nonplanar aromatic motif. For the planar motif, thiophene nucleus is used for its excellent electronic properties. The two structural units are joined through an acetylene linkage that allows for continuity of electronic communication through the structure. This interaction is found to be excellent in the first three oligomers of the series (C_1T_1, C_2T_1, and C_3T_2). In the last two soluble oligomers (C_3T_2 and C_4T_3), however, this property attenuates. This suggests that further modulation of the electronic properties may come from alteration of the chemical structure of the planar unit and the bridge and not through further extension of the oligomer length. For example, the acetylene unit can be replaced with a vinyl group and the thiophene can be replaced with a bis-thiophene, benzodithiophene, fluorene, or a carbazole moiety.[53,54] In light of the present results, it is probable that going to a polymeric structure (increasing the molecular length) will not help in modulation of the electronic properties any further. An important part of this study is also the finding that longer oligomers show a large two-photon absorption cross section as well as two-photon-excited bright luminescence. This is significant as corannulene and its derivatives are, so far, not known to exhibit excellent nonlinear optical properties. In essence, this work reports on hitherto unknown concept of including a nonplanar aromatic motif into the π-conjugated discrete materials, their synthetic feasibility, their photophysical properties and its implications on future research targets, and finally the discovery that corannulene derivative, when electronically extended, are capable of exhibiting the phenomena of nonlinear optical activity in an excellent manner. We believe that this report will entice further work on studying the effect of nonplanar aromatic component on the properties of otherwise planar π-conjugated materials.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b12468.

Synthesis and characterization details (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*mstuparu@ntu.edu.sg

ORCID ⓞ

Handong Sun: 0000-0002-2261-7103

Mihaiela C. Stuparu: 0000-0001-8663-6189

Author Contributions

#J.L. and A.T. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Davis, W. B.; Svec, W. A.; Ratner, M. A.; Wasielewski, M. R. *Nature* **1998**, *396*, 60.
(2) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350.
(3) Berresheim, A. J.; Müller, M.; Mullen, K. *Chem. Rev.* **1999**, *99*, 1747.
(4) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605.
(5) Fichou, D. *J. Mater. Chem.* **2000**, *10*, 571.
(6) Roncali, J. *Acc. Chem. Res.* **2000**, *33*, 147.
(7) de Bettignies, R.; Nicolas, Y.; Blanchard, P.; Levillain, E.; Nunzi, J. M.; Roncali, J. *Adv. Mater.* **2003**, *15*, 1939.
(8) Wilson, J. N.; Josowicz, M.; Wang, Y.; Bunz, U. H. F. *Chem. Commun.* **2003**, *24*, 2962.
(9) Meier, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 2482.
(10) Grimsdale, A. C.; Müllen, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 5592.
(11) Nielsen, C. B.; Angerhofer, A.; Abboud, K. A.; Reynolds, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 9734.
(12) Yang, X.; Dou, X.; Rouhanipour, A.; Zhi, L.; Räder, H. J.; Müllen, K. *J. Am. Chem. Soc.* **2008**, *130*, 4216.
(13) Amir, E.; Amir, R. J.; Campos, L. M.; Hawker, C. J. *J. Am. Chem. Soc.* **2011**, *133*, 10046.
(14) Kim, F. S.; Ren, G.; Jenekhe, S. A. *Chem. Mater.* **2011**, *23*, 682.
(15) Binauld, S.; Damiron, D.; Connal, L. A.; Hawker, C. J.; Drockenmuller, E. *Macromol. Rapid Commun.* **2011**, *32*, 147.
(16) Parkhurst, R. R.; Swager, T. M. *J. Am. Chem. Soc.* **2012**, *134*, 15351.
(17) Amir, E.; Murai, M.; Amir, R. J.; Cowart, J. S., Jr; Chabinyc, M. L.; Hawker, C. J. *Chem. Sci.* **2014**, *5*, 4483.
(18) Zhou, C.; Liang, Y.; Liu, F.; Sun, C.; Huang, X.; Xie, Z.; Huang, F.; Roncali, J.; Russell, T. P.; Cao, Y. *Adv. Funct. Mater.* **2014**, *24*, 7538.
(19) Schuster, N. J.; Paley, D. W.; Jockusch, S.; Ng, F.; Steigerwald, M. L.; Nuckolls, C. *Angew. Chem., Int. Ed.* **2016**, *55*, 13519.
(20) Wu, Y.-T.; Siegel, J. S. *Chem. Rev.* **2006**, *106*, 4843.
(21) Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868.
(22) Sygula, A. *Eur. J. Org. Chem.* **2011**, *2011*, 1611.
(23) Ayalon, A.; Rabinovitz, M.; Cheng, P. C.; Scott, L. T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1636.
(24) Eisenberg, D.; Quimby, J. M.; Jackson, E. A.; Scott, L. T.; Shenhar, R. *Chem. Commun.* **2010**, *46*, 9010.
(25) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 1920.
(26) Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 1921.
(27) Seiders, T. J.; Baldridge, K. K.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 517.
(28) Juríček, M.; Strutt, N. L.; Barnes, J. C.; Butterfield, A. M.; Dale, E. J.; Baldridge, K. K.; Stoddart, J. F.; Siegel, J. S. *Nat. Chem.* **2014**, *6*, 222.
(29) Miyajima, D.; Tashiro, K.; Araoka, F.; Takezoe, H.; Kim, J.; Kato, K.; Takata, M.; Aida, T. *J. Am. Chem. Soc.* **2009**, *131*, 44.
(30) Sygula, A.; Fronczek, F. R.; Sygula, R.; Rabideau, P. W.; Olmstead, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 3842.
(31) Xiao, W.; Passerone, D.; Ruffieux, P.; Aït Mansour, K.; Gröning, O.; Tosatti, E.; Siegel, J. S.; Fasel, R. *J. Am. Chem. Soc.* **2008**, *130*, 4767.
(32) Lampart, S.; Roch, L. M.; Dutta, A. K.; Wang, Y.; Warshamanage, R.; Finke, A. D.; Linden, A.; Baldridge, K. K.; Siegel, J. S. *Angew. Chem., Int. Ed.* **2016**, *55*, 14648.
(33) Yanney, M.; Fronczek, F. R.; Sygula, A. *Angew. Chem., Int. Ed.* **2015**, *54*, 11153.
(34) Stuparu, M. C. *Angew. Chem., Int. Ed.* **2013**, *52*, 7786.
(35) Stuparu, M. C. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 2641.
(36) Mack, J.; Vogel, P.; Jones, D.; Kaval, N.; Sutton, A. *Org. Biomol. Chem.* **2007**, *5*, 2448.
(37) Lu, R.-Q.; Zhou, Y.-N.; Yan, X.-Y.; Shi, K.; Zheng, Y.-Q.; Luo, M.; Wang, X.-C.; Pei, J.; Xia, H.; Zoppi, L.; Baldridge, K. K.; Siegel, J. S.; Cao, X.-Y. *Chem. Commun.* **2015**, *51*, 1681.
(38) Shi, K.; Lei, T.; Wang, X.-Y.; Wang, J.-Y.; Pei, J. *Chem. Sci.* **2014**, *5*, 1041.
(39) Fellows, W. B.; Rice, A. M.; Williams, D. E.; Dolgopolova, E. A.; Vannucci, A. K.; Pellechia, P. J.; Smith, M. D.; Krause, J. A.; Shustova, N. B. *Angew. Chem., Int. Ed.* **2016**, *55*, 2195.
(40) For extension of corannulene with a large planar aromatic system, see: Dutta, A. K.; Linden, A.; Zoppi, L.; Baldridge, K. K.; Siegel, J. S. *Angew. Chem.* **2015**, *127*, 10942.
(41) Jones, C. S.; Elliott, E.; Siegel, J. S. *Synlett* **2004**, *1*, 187.
(42) Wu, Y.-T.; Bandera, D.; Maag, R.; Linden, A.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **2008**, *130*, 10729.
(43) Stuparu, M. C. *Tetrahedron* **2012**, *68*, 3527.
(44) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **2000**, *122*, 6323.
(45) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467.
(46) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.
(47) Ho, H. A.; Brisset, H.; Elandaloussi, E. H.; Frère, P.; Roncali, J. *Adv. Mater.* **1996**, *8*, 990.
(48) Frère, P.; Raimundo, J.-M.; Blanchard, P.; Delaunay, J.; Richomme, P.; Sauvajol, J.-L.; Orduna, J.; Garin, J.; Roncali, J. *J. Org. Chem.* **2003**, *68*, 7254.
(49) Seiders, T. J.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7804.
(50) Siddle, J. S.; Ward, R. M.; Collings, J. C.; Rutter, S. R.; Porres, L.; Applegarth, L.; Beeby, A.; Batsanov, A. S.; Thompson, A. L.; Howard, J. A. K.; Boucekkine, A.; Costuas, K.; Halet, J.-F.; Marder, T. B. *New J. Chem.* **2007**, *31*, 841.
(51) Mishra, R.; Sankar, J. *RSC Adv.* **2013**, *3*, 10658.
(52) Xu, C.; Webb, W. W. *J. Opt. Soc. Am. B* **1996**, *13*, 481.
(53) Huang, P.; Du, J.; Biewer, M. C.; Stefan, M. C. *J. Mater. Chem. A* **2015**, *3*, 6244.
(54) Sista, P.; Biewer, M. C.; Stefan, M. C. *Macromol. Rapid Commun.* **2012**, *33*, 9.