Toward an Air-Stable Triradical with Strong Spin Coupling: Synthesis of Substituted Truxene-5,10,15-triyl

Xiao Yang, Di Zhang, Yinhui Liao, and Dahui Zhao*

ABSTRACT: With the aim to achieve air-stable polyradical species manifesting strong spin coupling, synthetic endeavors are made toward triradical molecules featuring a truxene-triyl skeleton. Commonly used steric-hindering side groups such as 2,4,6-trichlorophenyl and 9-anthracenyl are both found to be incompetent at stabilizing the targeted truxene triradical, which appears to be elusive from isolation and characterization. Nonetheless, single-crystal structures of adducts formed by relevant radicals are obtained, which strongly suggests the transient existence of the designed triradicals. Finally, a truxene triradical comprising 1-anthracenyl along with two 9-anthracenyl substituents is successfully isolated and found to exhibit decent stability in air. We propose that because of the smaller dihedral angle assumed by 1-anthracenyl with respect to the plane of truxene-triyl, more effective π-conjugation allows the spin density to be more widely delocalized and distributed to the anthracenyl side groups. Thus, higher stability is gained by the triradical molecule.

INTRODUCTION

Strong ferromagnetic or antiferromagnetic electron-coupling effects are widely manifested and studied with heavy atom-containing materials, which have presented promising potential for a range of unique applications, such as superconductors,\textsuperscript{1−3} single-molecule magnets,\textsuperscript{4−6} and spin liquids,\textsuperscript{7−9} pertinent to topological quantum computation.\textsuperscript{10} Nonetheless, such properties are far less explored with organic molecules because either weak spin coupling or low chemostability is typically observed with open-shell organic molecules.\textsuperscript{11−21} However, as widely demonstrated in the opto-electronic and semiconducting applications, besides the superior mechanical assets, organic materials prevailingly surpass inorganic counterparts in terms of their economic and environmental costs. Moreover, versatile methods are readily available for modifying the structures and fine-tuning the properties of various organic molecules, which further boost their application values.\textsuperscript{22−29} Thus, with the desire to induce and harness spin-related properties from organic molecules, the first order of issue arises to design and prepare air-stable organic polyradicals boasting a strong spin coupling effect.

In the past few years, the correlation between the spin-coupling strength and chemical structure of organic diradicals has attracted increasing attention. Wu et al. reported a series of tetracyano-oligo(N-annulated perylene)quinodimethane derivatives and found that with an increasing number of repeat units, the singlet–triplet energy gap ($\Delta E_{ST}$) with the conjugated molecule decreased gradually, suggesting a weakened antiferromagnetic coupling effect. As the conjugation length continued to extend, ferromagnetism became the dominating effect, indicating that less-definable intermolecular interactions likely prevailed as the intramolecular spin coupling diminished.\textsuperscript{30,31}

Based on these previous results, it appears that spins confined to a smaller conjugation area are favorable for fostering stronger intramolecular coupling. Simple 1,3,5-trimethylenebenzene is the smallest unit imaginably suitable for accommodating three spin electrons.\textsuperscript{32} However, as prior studies have also shown that torsion angles may sensitively influence the strength of spin coupling,\textsuperscript{33} additional covalent linkages are introduced to confer a nearly completely rigid framework and warrant a strong coupling effect. Thus, truxene-5,10,15-triyl becomes the obvious choice.\textsuperscript{34−36}

Nonetheless, unlike the simple 1,3,5-trimethylenebenzene, truxene-5,10,15-triyl allows additional conjugative paths for spin couplings, with which quinoidal resonance forms become viable, as shown in Figure 1. As such quinoidal forms apparently facilitate antiferromagnetic coupling among the
spins, the overall situation becomes more sophisticated than the case of 1,3,5-trimethylenebenzene. Previously, indeno[1,2-a]fluorene, which can be considered as a partial structure of truxene-5,10,15-triyl, was investigated by Haley et al. The molecule was shown more like a diradical than a quinoid molecule, with a radical character index calculated to be 0.8, as compared to 1 representing a pure diradical. This index value was noticeably higher than other indenofluorene isomers. The ground state of indeno[1,2-a]fluorene was revealed to be a triplet. A considerable zero-field splitting parameter of ca. 22 mT was estimated, larger than that reported for trimethylenebenzene (14 mT) and substituted m-xylene diradical (16 mT). As an interesting radical structure, not surprisingly, the synthesis of truxene-5,10,15-triyl was conceived earlier. Swager et al. attempted the synthesis of truxene-5,10,15-triyl decorated with mesityl groups, by reducing a corresponding triol precursor with SnCl2 under acidic conditions. Such conditions eventually afforded a dihydro-mono-radical product. A quinoidal structure was suggested to exist as an intermediate, which was then further reduced in the basic solution. This previous study nonetheless suggested that the truxene triradical molecule likely manifested strong spin coupling. In order to evade the problem of over-reduction occurring to the molecule, we designed alternative synthetic route to evade the problem of over-reduction occurring to the molecule likely manifested strong spin coupling. In order to evade the problem of over-reduction occurring to the molecule, we designed alternative synthetic route.

![Figure 1](https://dx.doi.org/10.1021/acs.joc.9b03077)

**Figure 1.** Triradical and quinoidal forms of truxene-5,10,15-triyl.

### RESULTS AND DISCUSSION

As evidenced by the optimal stability of tris(2,4,6-trichlorophenyl)methine, 2,4,6-trichlorophenyl (TCP) appears to be a favorable substituent offering competent protection to the radical site by virtue of both its steric and electronic effects. Unlike the mesityl group, the absence of benzylic hydrogen atom circumvents the radical eradication through hydrogen atom transfer mechanism. Hence, a truxene triradical molecule 1-TCP bearing three TCP substituents was designed, and its synthesis route as shown in Scheme 1 was examined. In order to obtain the hydrogenated precursor H-1-TCP, 1,3,5-tris(2′-formylphenyl)benzene (2) was first prepared by performing a Miyaura–Suzuki reaction between 1,3,5-tribromobenzene and (2-formylphenyl)boronic acid. Then, by slowly adding in situ prepared TCP lithium to a solution of 2 at −78 °C for 12 h, triol 3 was acquired with a decent yield of over 90%. Subsequently, this triol molecule was subjected to a triple intramolecular Friedel–Crafts (F–C) alkylation upon exposure to a Lewis acid of BF3·Et2O. The relatively low yield of H-1-TCP (50%) was mainly a result from the appearance of a side product featuring undesired cyclization regiochemistry rendering one of the three hydroxyl groups left unreacted.

![Scheme 1](https://dx.doi.org/10.1021/acs.joc.9b03077)

**Scheme 1.** Designed Synthesis of Tris(2,4,6-trichlorophenyl)-truxene-5,10,15-triyl

Then, we carried out the oxidation of H-1-TCP by sequential treatment with t-BuOK and p-chloranil, which afforded nearly quantitative formation of a brownish product, showing good air stability. High resolution mass spectrometry [matrix-assisted laser desorption ionization ion cyclotron resonance (MALDI-ICR)] revealed an ion peak matching the molecular mass of desired triradical 1-TCP. A narrow resonance signal was also detected by the electron paramagnetic resonance (EPR) spectroscopy, suggesting the paramagnetic property of the product around the room temperature. Nonetheless, when a single crystal grown from the mixed solvent of methanol and toluene was analyzed, an adduct structure 1′-OMe was identified (Figure 2). The crystallized molecule was not a radical, with the benzene ring saturated with two methoxy and a tert-butoxymethyl group. Such a structure strongly suggested that the TCPs protected the 5, 10 and 15 positions fairly well, but the central benzene ring evidently accommodated a significant portion of the spin density and became highly reactive. It was}

![Figure 2](https://dx.doi.org/10.1021/acs.joc.9b03077)

**Figure 2.** Proposed transformation from 1′-TCP to 1′-OMe during the growth of single crystals (single-crystal structure of 1′-OMe shown with hydrogen atoms omitted).
reasonable to assume that 1'-OMe was formed from 1'-TCP (Figure 2) during crystallization in the binary solvent containing methanol. Nonetheless, the tert-butoxy group was imaginably incorporated during the last step of reaction, in which t-BuOK was employed as a reagent. Nonetheless, the origin of the methylene unit was somewhat puzzling. Later, we found that the problem arose from the solvent contamination. The solvent used for carrying out the oxidation reaction, tetrahydrofuran (THF), was contaminated with methylene chloride and t-BuOH. The EPR and UV–vis spectra collected from the presumed 1'-TCP' were also consistent with a quinoidal-diradical hybrid structure (Figures S1 and S2). However, when we performed the final step of syntheses in properly purified anhydrous THF, although 1'-TCP was no longer detected, the desired product 1-TCP was unfortunately not attainable. We suspected that it was due to the insufficient stability of 1 around room temperature.

Although triradical 1-TCP was not isolated, the observed adducts 1'-TCP and 1'-OMe strongly suggested its transient existence under the applied reaction conditions. Moreover, the appearance of triple adduct 1'-OMe alluded to the diradical and triradical behaviors of 1'-TCP and 1-TCP, respectively. The diradical nature of 1'-TCP was consistent with the experimental characterizations of an analogue molecule, indeno[1,2-a]fluorene, previously reported by the Haley group. The triradical property of 1-TCP was confirmed by the theoretical calculation results (Figure 3). A doublet-quartet energy gap ($\Delta E_{\text{DQ}} = \Delta E_{\text{UDFT}} \times ((S_{\alpha}^2) - (0.5 \times 1.5))/( (S_{\alpha}^2) - (S_{\beta}^2))$) of 3.97 kcal mol$^{-1}$ was predicted for truxene-$5,10,15$-tryl without substituents. The density-functional theory (DFT) results further revealed that, besides the three positions of carbons $S$, 10 and 15, the central benzene ring shares a significant portion of the spin density distribution, which not only well explained the adduct structures of 1'-TCP and 1'-OMe, but also corroborated the strong spin coupling among the electrons.

Because 1-TCP did not exhibit adequate ambient stability, we designed structural modifications to help stabilize the molecule, by installing chlorine substituents around the truxene framework, as they were shown to impart favorable stabilizing effect to triphenylmethine-type radicals. The chlorine atoms were introduced to the peripheral benzene ring, at the para- and ortho-positions relative to carbon $S$, 10, and 15 to promote the resonance stabilizing effect. The synthesis of chlorine-substituted analogue 1-Cl is outlined in Scheme 2. The hexachloro-substituted tris-benzaldehyde 4 was also synthesized by Miyaura–Suzuki reaction, with the substrate obtained from a $\alpha$-bromination reaction of 2,4-dichlorobenzaldehyde, using the Pd-catalyzed C–H activation methodology. However, the subsequent nucleophilic addition to 4 with TCP lithium was not successful, likely due to the steric hindrance and/or side reactions such as lithium–halogen exchange. After screening a number of different protocols, we found that Lewis-assisted intermolecular followed by intra-molecular $F$–$C$ reaction between 4 and 1,3,5-trichlorobenzene could accomplish the assembly of the TCP-substituted truxene skeleton. However, in spite of all the efforts, the maximum yield of this tandem $F$–$C$ reaction was merely 10%. Interestingly, instead of the expected trihydro-product 3H-1-Cl, the $F$–$C$ alkylation conditions afforded a mono-radical molecule 2H-1-Cl. Although the exact mechanism is not clear to us, the formation of such a radical product evidently hinted the improved radical stability as a result of truxene framework chlorination, and it also explained the low reaction yield. Then, when subjected to the treatment ofaq. HI, this radical 2H-1-Cl could be reduced and converted to molecule 3H-1-Cl, the structure of which was confirmed by the $^1$H NMR spectroscopy.

Next, the deprotonation–oxidation reaction was performed with either 2H-1-Cl or 3H-1-Cl, and as expected the two reactants yielded the same product. The generated molecule displayed similar UV–vis absorption as 2H-1-Cl (Figure S1), and mass spectrometry [matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF)] detected only one

Figure 3. Calculated spin density distribution of truxene-$5,10,15$-tryl on UB3LYP/6-31+G(d,p) level using Gaussian 09 suites of programs (left: quartet state; right: doublet state).

Scheme 2. Designed Synthesis of Chlorine-substituted Truxene Triradical$^a$

\[\begin{align*}
&\text{B} + \text{S} \rightarrow \text{Spin} \rightarrow \text{Bpin} \\
&\text{4} \rightarrow \text{3H-1-Cl} \rightarrow \text{2H-1-Cl} \rightarrow \text{1-Cl (not isolable)}
\end{align*}\]

$^a$(i) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, THF/H$_2$O, 80 °C, 12 h, 50%. (ii) 1,3,5-trichlorobenzene, AlCl$_3$, 160 °C, 6 h, 10%. (iii) aq. HI, dichloromethane, r.t., 30 min, 92% (iv) (a) t-BuOK, THF, 50 °C, 6 h; (b) p-chloranil, THF, r.t., 5 min.

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molecular mass peak, which was consistent with the triradical structure. The EPR spectroscopy showed a single peak without hyperfine coupling, which offered limited structure information. However, treating this product with reductive aq. HI did not revert it back to the hydrogenated molecule 3H-1-Cl, but instead led to a less symmetric species with an unidentifiable structure based on its 1H NMR spectrum.

Again, the X-ray single-crystal structural analysis provided the unambiguous information. The crystal structure was actually an adduct (1'-BHT, Figure 4) of the expected 1-Cl with the oxidized product of BHT (butylated hydroxytoluene), which was a common stabilizer in commercially available THF. Again, like 1-TCP the addition took place with the central ring in 1-Cl, suggesting the spin density was still high in that region where it was relatively exposed. Then, we used BHT-free THF as the solvent to carry out the final step of 1-Cl synthesis, but unfortunately the triradical 1-Cl was still not isolable from the reaction mixture. Moreover, since the ion peak of 1-Cl was detected in the MALDI-TOF mass spectrum, we attempted to realize a retro-cycloaddition of 1'-BHT under photochemical conditions by illuminating 1'-BHT with a mercury or light-emitting diode lamp, but the adduct was decomposed under either radiation condition.

In retrospection, the fact that 1-TCP was also synthesized in the presence of BHT, but no corresponding BHT adduct to 1-TCP was detected, suggested that improved stability and longer lifetime was exhibited by 1-Cl compared to 1-TCP, although it was still not adequate to allow for isolation under ambient conditions. Namely, the strategy of decorating truxene with chlorine atoms made an insufficient yet noticeable difference in the radical stability. Since the addition consistently occurred to the central ring, further reducing the spin density seemed necessary. Wu et al. reported a series of persistent radical molecules featuring a protective group of 10-(3,5-di(tert-butyl)phenyl)anthracen-9-yl.47−49 We speculated that such a polycyclic aromatic substituent might be more effective at dispersing the spin through conjugation effect.

Again, the cascade F–C reactions were examined first with substrates 2 and 9-(4-(tert-butyl)phenyl)anthracene (An) to promote the formation of an An-substituted truxene scaffold (Scheme 3). Similar to the situation with 1-Cl, instead of the trihydro-precursor H-1-An, some bright green compound suspected to be the (mono-)radical species was formed. Thus, without separation, this product (mixture) was subjected to aq. HI, with the intention to reduce the radical species to H-1-An. Upon the reduction with HI, a number of different compounds were detected, which were unable to separate with silica gel flash column chromatography. Using the preparative size exclusion chromatography (SEC), the major components (H-1-An and H-1'-An) were isolated, which showed nearly identical Rf values on the thin-layer chromatography. This mixture was then subjected to reactions with t-BuOK followed by treatment with p-chloranil. A dark green substance was then isolated from the oxidation reaction. As evidenced by the mass spectrometry, its molecular mass matched with the desired tri-radical structure. Nonetheless, when this oxidation product was reduced by aq. HI it was converted back to the minor...
component in the precursor mixture, H-1′-An, rather than the major H-1-An. The structure of H-1′-An was then proposed based on its $^1$H NMR spectrum (Figure S6). Although this reduction result indicated that the oxidation product was still not the expected 1-An, the reversible redox process was nonetheless encouraging evidence corroborating that the oxidation product, later proven to be EPR active, was not an irreversibly formed covalent adduct, like 1′-BHT and 1′-TCP which could not be reverted to 3H-1-Cl and H-1-TCP.

In order to further elucidate the structures of H-1-An and H-1′-An, which constitute vital clues to the identity of the oxidation radical product, an isomerization protocol was conducted (Scheme 4). In the literature, by producing the tri-anionic state of a substituted truxene, the diastereomer mixture could be converged to the all syn-configuration and thus greatly simplified the $^1$H NMR spectrum. Upon such an isomerization process, the $^1$H NMR spectroscopy clearly confirmed the structure of syn-H-1-An (Supporting Information), by which the structure of H-1-An was substantiated. On the other hand, the results from these experiments also revealed that H-1′-An was not a diastereomer of H-1-An, as it was not convertible to syn-H-1-An. Finally, by carefully examining the $^1$H NMR spectrum, making proper chemical shift assignments to the signature protons and collecting information from the mass spectrometry, the structure of H-1′-An was identified (Figure S6). That is, likely due to the steric hindrance, a small portion of the phenylanthrancene used its carbon 4, instead of 9, to perform the nucleophilic attack to carbon 2, and hence produced an asymmetric truxene product H-1′-An (Scheme 3). Moreover, it was found that, during the reduction enabled by aq. HI, some of the radical species was over-reduced to 3H-1′-An by incorporating two additional hydrogen atoms. This partially de-aromatized molecule presented more easily identified signature $^1$H resonances and helped endorsing the structure of H-1′-An, and thus 1′-An as well (Figure S7). The mass spectrometry of all relevant compounds also verified their respective structures. It was however worth noting that, in spite of the obtinment of 1′-An, the expected 1-An was not detected or isolated, although H-1′-An was unmistakably generated from the F−C reactions. We suspected that this was due to the lower stability of 1-An compared to 1′-An under similar conditions.

In subsequent electrochemical characterizations, the differential pulse and cyclic voltammetry (CV) techniques clearly revealed triple reduction and triple oxidation processes, which helped confirming the triradical structure of 1′-An (Figure 5). Next, the EPR experiments unambiguously evidenced the radical nature of 1′-An. While a broad, featureless resonance peak was recorded by the EPR spectroscopy from a solution at room temperature (Figure S4), a zero filed splitting signature indicating high spin species was clearly identifiable with 1′-An in the solid state (Figure 5). Nonetheless, a low spin concentration of less than one spin per molecule was observed, which likely resulted from relatively strong antiferromagnetic intermolecular interactions among 1′-An. A variable-concentration experiment confirmed this hypothesis by showing an increased spin concentration upon diluting a solution of 1′-An in toluene (Figure S5). At a lower temperature, the EPR signal from solution exhibited much more sophisticated splitting. All these results suggested that certain complexes might even be formed at reduced temperatures (Figure S4). Similar phenomena of complex species were previously observed with other polycyclic aromatic hydrocarbon radicals.

It was intriguing that, while 1′-An exhibited decent air stability by showing a slow decomposition over 2 days in solution under ambient conditions, we were not able to isolate or even detect 1-An bearing three 9-anthracenyl side groups. We assumed this suggested the far lower stability of the latter than the former. In terms of the steric effect, 9-anthracenyl should evidently be more effective at shielding the radical site than a 1-anthracenyl. We hence suspected that 1-anthracenyl, being less steric-hindering on one side, was more effective at stabilizing the radical by assuming a smaller dihedral angle relative to the truxene plane and thus being more competent at delocalizing the spin density through $\pi$-conjugation. To examine this hypothesis, DFT calculations were conducted to evaluate the structural difference of 1- and 9-anthracenyl substituted truxene moieties. As shown in the optimized structures (Figure 6), the dihedral angle between 9-anthracenyl and truxene moiety was 80.6°, while this angle was reduced to 67.5° in the 1-anthracenyl-substituted analogue. We speculate that the smaller dihedral angle effected more efficient $\pi$-conjugation and allowed a greater port of the spin to be...
delocalized to 1-anthracenyl, which helped reduce the spin density in truxene and stabilize the triradical. A substantial radical feature of the 1-anthracenyl group was also evidenced by the experimental result that the ΔH reduction experiment the 1 and 4 positions of 1-anthracenyl unit in 1'-An could be reduced. Additionally, the intermolecular antiferromagnetic interactions among 1'-An most likely also contributed to its superior stability. The 1-anthracenyl side group might as well play an important role in allowing for such intermolecular interactions to occur.

### CONCLUSIONS

A series of synthetic endeavors were made at synthesizing a truxene-5,10,15-triyl radical molecule. Different substituents including TCP and 10-(4-((tert-butyl)phenyl)anthracen-9-yl) were employed to shield and protect radical sites in the truxene scaffold. With the trichlorophenyl substituents, the radical molecules appeared to be fairly reactive with its central ring, which accommodated partial spins from all three radicals, by forming different adducts with trace amounts of impurities from the reaction solutions. Decorating the peripheral positions of truxene with chlorine atoms helped stabilize the structure but was insufficient to confer a persistent triradical under ambient conditions. By switching from TCP to 9-anthracenyl substituents, the corresponding truxene-5,10,15-triyl was still not isolable. Nevertheless, a serendipitously obtained truxenetriyl 1'-An, featuring two 9-anthracenyl and one 1-anthracenyl substituents, was isolated and found to possess superior stability in air. We speculate that the moderate steric hindrance of 1-anthracenyl allowed for better π-conjugation between the truxene skeleton and the anthracene side group and was hence more competent at delocalizing and sharing the spin density. Thereby, the triradical was better stabilized. The electrochemical characterization supported the triradical structure of 1'-An by demonstrating the triple oxidation/reduction processes and the EPR experiment also confirmed the paramagnetic nature of the molecule. Nonetheless, the magnetic property studies also suggested that 1'-An experienced significant intermolecular antiferromagnetic interactions. These intermolecular antiferromagnetic interactions, which might as well have benefitted from the smaller steric hindrance conferred by the 1-anthracenyl side group, have in all probability contributed to the favorable stability observed with 1'-An. More in-depth studies on the structures and magnetic properties of more diverse triradical molecules are being carried out and will be reported in due course.

### EXPERIMENTAL SECTION

#### General Procedures

All reactions were performed with oven-dried glassware under a nitrogen atmosphere unless specified. T-BuOK was sublimed before use. All solvents were redistilled over Na except for commercially obtained super-dry solvents. All reactions that require heating were performed in an oil bath. 1H and 13C NMR were performed with a Bruker ARX400 NMR spectrometer, and EPR was conducted with a Bruker EMXplus CW X-Band EPR spectrometer. The UV-vis spectra were recorded on a HITACHI U4100 UV-vis spectrometer. MALDI-TOF was performed with an AB Sciex 5800 MALDI-TOF/TOF system. The ESI-ICR and MALDI-ICR were performed on a Rigaku XtALAB PRO 007HF(Mo) single-crystal X-ray diffractometer. Preparative SEC was conducted with a JAI LabACE LC-5040 Recycling Preparative HPLC with a JAIAGEL-2HR column. 1,3,5-Trichlorobenzene, 9-bromoanthracene, (4-(tert-butyl)phenyl)-boronic acid, 1,3,5-tribromobenzene, and 2-bromobenzaldehyde were obtained from commercial resources and used as received. 2-Bromo-4,6-dichlorobenzaldehyde was synthesized according to the protocol previously reported by Fabić, and 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene was synthesized using 1M solution of 1,1-diphenyl-2-picrylhydrazyl in toluene (0.84 mmol mL\(^{-1}\)) as the supporting electrolyte. The potential was externally calibrated against ferrocene/ferrocenium. The scan rate was 100 mV/s for CV, and the following conditions were applied to DPV: increase E(V) = 200 mV, amplitude = 50 mV, pulse width = 0.05 s, sample width = 0.0167 s, pulse period = 0.5 s, and quiet time = 1 s, sensitivity (A/V) = 1 × 10^{-5}.

#### Compound 2 (5′-(2-Formylphenyl)-1′,3′;1′-terphenyl)-2′,2″-dicycloaldehyde)

To a 250 mL Schlenk tube containing 1,3,5-tribromobenzene (2.10 g, 6.67 mmol), (2-formylphenyl)boronic acid (740 mg, 4.03 mmol), CuCl (3.51 mg, 0.032 mmol), and NaOAc (1.16 g, 14.7 mmol) in 40 mL CHCl3 was added Ph2SiCl3 (400 μL, 2.1 g). The mixture was stirred for 3 h, then filtered and washed with H2O and MeOH to obtain a white solid. The white solid was collected by filtration and washed with H2O and MeOH to obtain white solid. The white solid was then dried under vacuum at 60 °C, leading to a yellow solid. The yield was 0.61 g (87%). The NMR and MS data are consistent with the expected compound.

#### Compound 3 (3,5-Di(2-hydroxy(phenyl)methyl)(phenyl)-phenyl-l-phenylmethanone)

Under a nitrogen atmosphere at ~78 °C, n-BuLi (3.0 mL, 2.4 M) was added to a solution of 1,3,5-trichlorobenzene (1.30 g 7.17 mmol) in THF (40 mL) in a Schlenk tube. The reaction mixture was then allowed to stand at ~50 °C for 15 min, before a solution of 2 (350 mg, 0.896 mmol) in THF (10 mL) was then transferred to it via a needle. The mixture was maintained at ~60 °C for 12 h, quenched with water at a lowered temperature, and then reacted with ethyl acetate (50 mL) three times. The combined organic layers were washed with saturated NaCl and saturated brine, dried with anhydrous Na2SO4, and concentrated under reduced pressure to obtain a mixture of 1,3,5-trichlorobenzene (4.93 g 9.27 mmol). The mixture was then stirred at r.t. for 10 min before quenching with H2O (50 mL) followed by extraction with dichlormethane (100 mL).

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**Figure 6.** Optimized structures of fragments of 1′-An (left) and 1-An (right) on UB3LYP/6-311G(d,p) level.
three times. The combined organic layers were washed with aq. NaHCO₃ and saturated brine, dried with anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified with flash chromatography of silica gel and eluted with PE (petroleum ether)/CH₂Cl₂ (6:1, v/v) to afford H-1-TCP (410 mg, 52% for 2 steps). Rf = 0.7 (PE/CH₂Cl₂, 4:1, v/v). H NMR (400 MHz, CDCl₃): δ 7.71–7.65 (m, 3H), 7.49–7.35 (m, 6H), 7.34–7.22 (m, 6H), 7.08–7.03 (m, 2H), 7.02–6.98 (m, 1H), 6.54 (s, 1H), 6.45 (s, 1H), 6.39 (s, 1H). 13C{H} NMR (101 MHz, CDCl₃): δ 144.3, 144.2, 141.4, 140.4, 140.1, 138.3, 138.6, 138.0, 137.3, 137.1, 135.9, 135.6, 135.4, 133.2, 133.6, 133.5, 134.3, 130.2, 130.1, 128.4, 128.7, 127.6, 127.6, 127.0, 124.3, 124.2, 124.1, 121.1, 121.5, 121.0, 121.0, 119.9, 110.1, 97.0, 47.0. Anal. Calcd for C₅₇H₅₂Cl₂N₂O: C, 83.8; H, 5.6. Found: C, 83.7; H, 5.8.

Compound 4 (3.3',5',5'-Tetrachloro-5-(3,5-dichloro-2-formylphenyl)-1,3',5',3'-terphenyl-2,2'-dicarboxaldehyde). To a 100 mL Schlenk tube containing 1,3,5-tri(4,5,5-trimethyl-1,3,3-dioctadecyl-2-yl)benzene (200 mg, 0.439 mmol) and 2-bromo-4,6-dichlorobenzaldehyde (668 mg, 2.63 mmol), Pd(PPh₃)₄ (51 mg, 0.044 mmol) and K₂CO₃ (363 mg, 2.63 mmol) were added to THF (40 mL) and H₂O (4 mL) under a nitrogen atmosphere. The mixture was stirred at 80 °C in an oil bath for 8 h and then treated with ethyl acetate (50 mL) three times. The combined organic layers were washed with aq. NH₄Cl and brine and then concentrated under reduced pressure. The residue was purified with flash chromatography of silica gel and eluted with PE/CH₂Cl₂ (1:3, v/v) to afford 4 (130 mg, 50%). Rf = 0.4 (CH₂Cl₂). H NMR (400 MHz, CDCl₃): δ 10.25 (s, 3H), 7.54 (d, J = 2.0 Hz, 3H), 7.57 (d, J = 2.0 Hz, 3H), 7.24 (s, 3H). 13C{H} NMR (101 MHz, CDCl₃): δ 189.6, 145.2, 138.9, 137.8, 137.2, 130.5, 130.1, 129.9, 129.5. HRMS (ESI-ICR) m/z: [M + Na⁺]⁺ calcd for C₆₀H₄₂Cl₂NaO₃, 616.8810; found, 616.8810.

2H-1-Cl (1,3,6,8,11,13-Hexachloro-10,15-tris(2,4,6-trichlorophenyl)-10,15-dihydro-5H-diindenophenanthracene52 (1,2'-a:1',2'-cfluorene57). A mixture of 4 (100 mg), AlCl₃ (100 mg), and 1,3,5-trichlorobenzene (90 g) was heated in a sealed tube at 170 °C in an oil bath for 6 h. The reaction mixture was then cooled and extracted with dichlormethane (100 mL) three times. The combined organic layers were washed with aq. NaHCO₃ and brine and concentrated under reduced pressure. The residue was then sublimed to remove the excess 1,3,5-trichlorobenzene and then purified with flash chromatography of silica gel and eluted with PE to afford 2H-1-Cl (12 mg, 10.5%).

3H-1-Cl (anti-1,3,6,8,11,13-Hexachloro-5,10,15-tris(2,4,6-trichlorophenyl)-10,15-dihydro-5H-diindenophenanthracene52 (1,2'-a:1',2'-cfluorene57). To a solution of 2H-1-Cl in dichloromethane (20 mL), was added aq. HCl (2 mL) and stirred at rt for 30 min. The reaction mixture was then extracted with dichloromethane and the organic layer was washed with aq. Na₂SO₄ followed by brine and then concentrated under reduced pressure to afford 3H-1-Cl (11 mg, 92%). Rf = 0.7 (PE/CH₂Cl₂, 3:1, v/v). H NMR (400 MHz, CDCl₃): δ 7.82 (d, J = 1.8 Hz, 1H), 7.80 (d, J = 1.8 Hz, 1H), 7.73 (d, J = 1.8 Hz, 1H), 7.59 (t, J = 2.3 Hz, 2H), 7.58 (d, J = 2.2 Hz, 1H), 7.25 (d, J = 1.7 Hz, 1H), 7.23 (t, J = 1.8 Hz, 2H), 7.65–6.98 (m, 3H), 6.40 (s, 1H), 6.35 (s, 1H), 6.30 (s, 1H).

H-1-An and H-1-An'. To a solution of compound 2 (100 mg, 0.256 mmol) and 9-(4-(tert-butyl)phenyl)anthracene36 (397 mg, 1.28 mmol) in Ac₂O (1 mL) and dried dichloromethane (50 mL), was added triflic acid (TIOH, 0.04 mL). The mixture was stirred for 10 min at 40 °C in an oil bath and then concentrated to afford 3H-1-Cl (11 mg, 92%). Rf = 0.7 (PE/CH₂Cl₂, 3:1, v/v). H NMR (400 MHz, CDCl₃): δ 7.82 (d, J = 1.8 Hz, 1H), 7.73 (d, J = 1.8 Hz, 1H), 7.59 (t, J = 2.3 Hz, 2H), 7.58 (d, J = 2.2 Hz, 1H), 7.25 (d, J = 1.7 Hz, 1H), 7.23 (t, J = 1.8 Hz, 2H), 7.65–6.98 (m, 3H), 6.40 (s, 1H), 6.35 (s, 1H), 6.30 (s, 1H).

H-1-An (5,10,15-Tris(10-(4-(tert-butyl)phenyl)anthracen-9-yl)-10,15-dihydro-5H-diindenophenanthracene52 (1,2'-a:1',2'-cfluorene57). Under a nitrogen atmosphere, t-BuOH (5 mL) was added to H-1-An (50 mg 0.039 mmol) and t-BuOK (100 mg, 0.893 mmol) in a Schlenk tube. The reaction mixture was stirred at 100 °C in an oil bath for 24 h before quenching with water. Upon extraction with dichloromethane, the organic layer was washed with water and concentrated under reduced pressure to afford H-1-An without further purification (49 mg, 98%). Rf = 0.6 (PE/CH₂Cl₂, 3:1, v/v). H NMR (400 MHz, CDCl₃): δ 9.02 (d, J = 9.1 Hz, 3H), 7.92 (d, J = 8.8 Hz, 3H), 7.73 (t, J = 7.7 Hz, 3H), 7.62–7.48 (m, 13H), 7.37 (d, J = 8.1 Hz, 3H), 7.35–7.27 (m, 8H), 7.19 (d, J = 7.6 Hz, 3H), 7.12 (d, J = 7.7 Hz, 3H), 7.04 (s, J = 3.4 Hz, 3H), 6.89 (t, J = 7.5 Hz, 3H), 6.85–6.74 (m, 6H), 6.62 (t, J = 7.6 Hz, 1H), 1.46 (s, 27H). MS (MALDI-TOF) m/z: [M⁺]⁺ calcd for C₅₀H₄₀, 826.61; found, 826.61.
(70 mg, 0.284 mmol) was added to it under nitrogen atmosphere and stirred for 3 min. Upon condensation under reduced pressure, the residue was recrystallized in a solvent mixture of dichloromethane and CH3CN. The crystals were collected and purified by preparative TLC eluted with PE/CH2Cl2 (5:1 for 1-TCP and 1-Cl, and 3:1 for 1′-An). 

\[ \text{1′-An, Rf = 0.7} \text{ (hexane/CH2Cl2 3:1 v/v). MS (MALDI-TOF) m/z: [M]+ calcd for C99H75, 1263.59; found, 1263.45.} \]

**REFERENCES**


**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acs.joc.9b03077.

X-ray crystallography data, UV–vis and EPR spectra, NMR spectra, and computational data (PDF)

Crystallographic data (CIF)

Crystallographic data (CIF)

**AUTHOR INFORMATION**

Corresponding Author

Dahui Zhao — Beijing National Laboratory for Molecular Sciences, Centre for Soft Matter Science and Engineering, Key Lab of Polymer Chemistry & Physics of the Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China; orcid.org/0000-0002-4983-4060; Email: dhzhao@pku.edu.cn

Authors

Xiao Yang — Beijing National Laboratory for Molecular Sciences, Centre for Soft Matter Science and Engineering, Key Lab of Polymer Chemistry & Physics of the Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

Di Zhang — Beijing National Laboratory for Molecular Sciences, Centre for Soft Matter Science and Engineering, Key Lab of Polymer Chemistry & Physics of the Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

Yinhui Liao — Beijing National Laboratory for Molecular Sciences, Centre for Soft Matter Science and Engineering, Key Lab of Polymer Chemistry & Physics of the Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

Complete contact information is available at:

https://pubs.acs.org/10.1021/acs.joc.9b03077

Author Contributions

The manuscript was written through contributions of all authors.

Notes

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**REFERENCES**