

C₃-Symmetric Indole-Based Truxenes: Design, Synthesis, and Photophysical Studies

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 ABSTRACT:
 In recent years, truxenes and related polyaromatic
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Abstract: In recent years, truxenes and related polyaromatic hydrocarbons (PAHs) have engrossed ample interest of the scientific community because of their ease of synthesis, functionalizations, and use as building blocks for the synthesis of fullerene fragments, liquid crystals, larger polyarenes, and C_3 -tripod materials. In the present work, we have disclosed an ingenious method for the construction of various indolo-truxene hybrid molecules in good yields (52–90%), by means of the acid-catalyzed cotrimerization, Friedel–Crafts acylation, and Fischer indole synthesis, and fully characterized them through the standard spectroscopic techniques. The photophysical properties of the thusprepared compounds have also been investigated using steady-state



absorption and fluorescence and time-resolved fluorescence spectroscopy techniques. Moreover, the density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations have been studied to correlate them with the measured photophysical properties of the synthesized indolo-truxene derivatives.

1. INTRODUCTION

Over the last few decades, star-shaped polyaromatic hydrocarbons (PAHs) have attracted considerable research attention due to their diverse promising applications.¹⁻⁶ Particularly, truxene (10,15-dihydro-5*H*-diindeno[1,2-a;1',2'-c]fluorene) and its isomer, namely, isotruxene scaffold, have drawn significant attention because of their easy synthesis, high thermal stability, and availability of several tunable peripheral (e.g., C2, C7, & C12) positions besides three functionalizable methylene sites (e.g., C5, C10, and C15).^{7,8} Recently, several π -extended diindolotriazatruxene compounds have been synthesized and found to be promising materials for hole mobility in planar perovskite solar cells.⁵ Moreover, spiro-fused ladder-type oligo(*p*-phenylene)s were found to exhibit efficient multiphoton absorption and consequent fluorescence upconversion and stimulated emission due to the unification of high absorption cross section and high photoluminescence quantum yield.⁴ The photophysical and lasing characteristics of truxene core-based starburst-conjugated molecules (TrXD) with diphenylamine end-capper were examined, and the results have been compared with their analogues without diphenylamine moieties.⁶ However, these vital polyaromatic hydrocarbon molecules produce smart organic materials for promising applications in varied fields such as sensing, catalysis, solar cells, gas storage, and separation techniques.^{9–18}

Remarkably, substitution of carbon atom(s) in PAHs by the heteroatom(s) like N, O, or Si induces atypical changes in the geometry and/or optoelectronic signatures of the corresponding architectures.^{19–29} For instance, changing the bridging

carbon atom(s) of the truxene scaffold with N-atom(s) boosts its charge carrier mobility (Figure 1).^{30,31} Consequently, since the discovery of the triazatruxene (TAT, 2) in the year 1978 by Bergman and Egestad,³² TAT and its congeners that consist of three carbazole subunits fused onto a common central benzene ring in a planar C_3 -symmetric manner have exceptionally been used in numerous organicbased electronics materials.³³

Importantly, π -extended conjugation in the TAT as well as truxene molecules facilitates the hole extraction and $\pi - \pi$ intermolecular interactions; besides, it also increases the hole transport phenomena.^{34–36} More importantly, incorporation of the alkyl chains to the nitrogen atoms offers good solubility to the TAT molecule, and concurrently, they shelter the "perovskite layer" from the moisture because of their hydrophobic nature.³⁷ Furthermore, TAT scaffold is thought to be the best building block for organic photovoltaics, organic field-effect transistors, and organic light-emitting diodes due to its chemical versatility and easy adjustment of its electronic as well as optical properties.^{18,38,39} Interestingly, TAT derivatives have truly been used as hole-transport materials (HTMs) for

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Figure 1. Polycyclic aromatic hydrocarbons (top) and indole-based C₃-systems (bottom).

perovskite solar cells—reaching outstanding photoelectric conversion efficiencies (PCEs) up to 20.3%.^{31,37,40-42}

Notably, in addition to the TATs, various other heteroderivatives of truxene have also been reported along with their physiochemical properties and/or diverse potential applications.⁴³ It can be inferred from the literature that, undoubtedly, truxenes, isotruxenes, azatruxenes, and other heterocongeners remained among the most fascinating classes of PAHs because of their unique optical/electronic properties and planar C_3 symmetric structures.^{3,44–46}

On the other hand, indole has been unearthed as a vital heterocyclic scaffold because of its existence in numerous natural products and also the promising applications of indole-based compounds in pharmaceuticals.^{47–51} Moreover, indole-3-carbinol and 3,3'-diindolylmethanes have been noticed to induce apoptosis in *"cancerous cells,"* whereas a plethora of bis-(indolyl) alkanes have been found in numerous bioactive metabolites of terrestrial/marine origin.⁵² Remarkably, to date, several indole-based drugs are present in the world market, and many hundreds are under clinical trials, creating curiosity among the scientific community worldwide to synthesize a diversified indole derivatives.

Therefore, bearing the enormous importance of both truxenes and indole systems^{53–55} in mind, herein we indented to prepare truxene-based C_3 -symmetric star-shaped hybrid molecules containing indole scaffolds logically around the truxene periphery. To the best of our knowledge, this is for the first time where indole chromophores have been linked in the peripheral of the truxene scaffold with the Fischer indole synthesis as a key step. Gratifyingly, three indole moieties fused onto the benzene ring, i.e., *aza*-truxene (2) and its congeners, have already been explored for diverse promising applications.^{7,56} We believe that the indolo-truxenes reported in the present investigation might find some valuable uses in the near future. A list of truxene and its heteroanalogues along with the C_3 -symmetric indole derivatives is displayed in Figure 1.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization. Toward the achievement of our goal for assembling several indolo-truxene derivatives (17, 18, 20, 22, and 24), we commenced with the preparation of already reported hexabutylated truxene (HexBT) derivative 14 by employing the reported procedure (Scheme 1).⁵⁷ Having the HexBT 14 in hand, it was cleanly transformed into the unknown truxene-centered tricarbonyl compound 10 in excellent yield (98%) utilizing a very wellknown 3-fold Friedel-Crafts acylation reaction in the presence of propionyl chloride and aluminum chloride (AlCl₃) in dichloromethane (DCM) solvent (Scheme 1).58,59 Next, we attempted to convert the truxene-tris(propan-1-one) 10 into the triindolo-truxene 12 using phenylhydrazine derivative 11 through an extremely popular Fischer indole strategy in green condition using deep eutectic solvents (DESs) under the consideration, but our all efforts in this direction were completely futile (Table 1, entries 1-3). The main reason for this failure was the solubility issue of the starting materials in the DESs, and the ketone 10 was recovered as such. Therefore, we switched our attention toward the conventional acid-induced Fischer indole synthesis protocol of 10 with phenylhydrazine; (a) using ZnCl₂/toluene, no desired product was formed; the reason for this failure is not yet clear (Table 1, entries 4) and (b) fortunately in the presence of p-TsOH/ EtOH, we successfully obtained the anticipated indolo-truxene in 90% yield (Table 1, entries 5). To further expose the scope of the 3-fold Fischer indolization (FI) in the construction of C₃-symmetric truxene-based systems, we used different phenylhydrazine derivatives (16, 21, and 23) to generate the corresponding indolo-truxenes (17, 22, and 24), respectively, in good yields (Scheme 1). Moreover, the indole-based truxene derivative 17 was transformed into the trimethylated indolotruxene derivative 18 in a decent yield (87%) using MeI/NaH in DMF (Scheme 1). Thus, prepared compounds were fully characterized by means of NMR spectroscopy as well as highresolution mass spectrometry/Q-TOF MALDI (see the Supporting Information (SI)). The mechanistic insight for the formation of indole scaffold through the classic Fischer





indole synthesis is well established in the scientific literature.⁶⁰ Taking the same into concert, as can be inspected from Scheme 2, herewith we report a protic acid-induced mechanistic route for the construction of the indole-based truxenes. To summarize, first of all there is a formation of an intermediate trihydrazone (27) from the tricarbonyl compound (26) and phenylhydrazine derivative (25) under acidic conditions. Next, the intermediate hydrazone (27) underwent a 3-fold enolization (*ene-amine tautomerism*) followed by a 3-fold [3,3]-sigmatropic rearrangement to furnish another intermediate compound (29) via 28. Afterward, aromatization of 29 followed by protonation and cyclization afforded compound 31, which upon elimination of NH₃ molecules delivers the anticipated truxene-based indole derivative 32.

2.2. Steady-State Absorption and Fluorescence Studies. To understand the excited-state behavior of the synthesized truxene derivatives, steady-state absorption and emission spectra have been recorded in dilute solutions of DCM. The absorption and emission spectra of all the compounds are shown in the left panel (top-to-bottom) of Figure 2. Absorption maxima in the ultraviolet (UV) region

around 300 nm are the hallmark of the truxene core due to the $\pi - \pi^*$ transition.^{15,61} In this study, the compounds exhibit a strong absorption band at a longer wavelength around the 330–350 nm region due to the π -conjugation in the molecular framework of all the truxene derivatives. It is observed that compound 10 has the lowest conjugation, and hence it shows the absorption peak at the shortest wavelength. However, it has been previously reported that thiophene and fluorene ethynylene functionalized truxene derivatives exhibit absorption bands at 340 and 350 nm, respectively, with well-defined vibronic properties.^{35,36} The emission spectrum of each compound is recorded by excitation at its maximum absorption wavelength. Compounds 20, 17, and 22 exhibit two peak maxima at around ~382 and ~405 nm, indicating a signature of vibronic feature. The emission maxima for compounds 10, 24, and 18 have been observed at \sim 396, \sim 406, and \sim 402 nm, respectively. According to the previous reports, the thiophenefunctionalized truxene derivative exhibits an emission peak at ~365 nm, while fluorene ethynylene functionalized truxene exhibits emission at 380 and 400 nm. The significant red shift in absorption and emission spectra indicates that the present



Scheme 2. Proposed Mechanistic Pathway for the Acid-Mediated Fischer Indole Synthesis



indole functionalized truxene derivatives form an enhanced π -delocalization, as was found in thiophene and fluorene ethynylene functionalized truxene derivatives.^{35,36} Note here that in the present case, compound **10** has no indole functionalization. Although it exhibits low absorption maxima, it shows a very broad and red-shifted emission band. The presence of carbonyl groups in the truxene core may impart charge transfer character in the excited state, which may be the source of the broad emission band in this compound 10. We have also carried out solid-state fluorescence measurements where it was found that the peak maxima appear at longer wavelengths than in the solution phase (see SI, Figure S1). The observed red shift is due to intermolecular interactions in the solid state.

2.3. Fluorescence Lifetimes. The fluorescence intensity decays for all the samples, collected using a 320 nm pulsed light-emitting diode (LED) excitation source, are shown in the

right panel (top-to-bottom) of Figure 2. The decays for compounds 20, 22, and 24 are found to be single exponential in nature, whereas the decays of the remaining compounds (10, 17, and 18) exhibit biexponential behavior. The decay fitting parameters are shown in Table 2. Compounds 10, 22, and 24 display a lifetime in the range of 1.2-1.7 ns, but the other compounds exhibit a shorter time component that is less than the instrument response function (IRF ~ 0.8 ns) along with a longer time component (0.8-1.2 ns). It may be noted here that the iterative reconvolution fitting method can capture shorter time components than IRF with reasonable accuracy. However, the relative amplitude associated with the longer time component is minimal (2 to 7%) for the compounds that exhibit biexponential decay. Compounds 17 and 18 contain heavy atoms (e.g., Br), and shorter lifetime components of 330 and 430 ps are found for these indolo-truxene derivatives, respectively. The significant decrease in the lifetime of these



Figure 2. In the left panel, steady-state absorption (blue) and emission (red) spectra are shown, and in the right panel, data from time-correlated single photon counting (TCSPC) are displayed. Excitation wavelength is 320 nm in all cases, and emission wavelengths are provided in Table 2.

Table 2. Steady-State Absorption (λ_{abs}), Molar Extinction Coefficient (ε), Emission (λ_{em}), and Fluorescence Lifetime (τ) Data of Indole-Truxene Derivatives

compound	λ_{abs} (nm)	$\varepsilon ~(\mathrm{M^{-1}~cm^{-1}})$	$\lambda_{\rm em}~({\rm nm})$	τ_1 (ps)	<i>a</i> ₁	$ au_2$ (ps)	<i>a</i> ₂	χ^2
10	334	92,000	425	110	0.98	1220	0.02	1.00
20	351	158,000	406	1461				0.99
17	350	217,000	405	330	0.96	800 ^a	0.04	0.96
24	337	111,000	409	1714				0.96
22	350	142,000	402	1257				1.00
18	335	123,000	405	430	0.93	1255	0.07	0.95
^a This time was fix	ed during fitting	<i>y</i> .						

Br-containing compounds as compared to others can be attributed to the enhancement of nonradiative intersystem crossing (ISC) with spin-orbit coupling. Moreover, compound **10** (containing the carbonyl group) shows a fast lifetime component of \sim 110 ps, which is beyond the scope of the

instrumental resolution. This indicates that the presence of a carbonyl group in the compound might play an important role in the dynamics of the excited state.¹⁵ It may be mentioned here that many truxene compounds have previously been used as potential materials in the production of aqueous organic



Figure 3. DFT-calculated structures of the synthesized indolo-truxene derivatives.

LED (OLED) devices due to their high photoluminescence and electroluminescence quantum yields. Such possibilities may be the subject of future research for the present indolebased truxene compounds.

2.4. Computational Study. Molecular structures of the thus-synthesized truxene derivatives were subjected to optimization to the global minima by using density functional theory (DFT). Calculations were carried out using the Gaussian 09 software package.⁶² Becke 3-parameter Lee–Yang–Parr (B3LYP) hybrid functional and 6-311G basis set have been used for all the calculations.⁶³

Figure 3 presents the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) for all six molecules. The energy values of the HOMOs and LUMOs are tabulated in Table 3, as eV unit. It was observed that the band gap of truxene-indole derivatives (17, 18, 20, 22, 24) was in the range of 3.864–4.272 eV,

Table 3. Data of the HOMOs and LUMOs along with Their Gap in eV

compound	molecular formula	E _{HOMO} (eV)	$E_{\rm LUMO}$ (eV)	$E_{\rm LUMO} - E_{\rm HOMO}$ (eV)
10	$C_{60}H_{78}O_3$	-6.285	-2.258	4.027
20	$C_{78}N_3H_{87}$	-5.469	-1.605	3.864
17	$C_{78}N_{3}H_{84}Br_{3}$	-6.095	-1.850	4.245
24	$C_{81}N_3H_{93}$	-5.823	-1.551	4.272
22	$C_{78}N_{3}H_{84}Cl_{3}$	-5.741	-1.877	3.864
18	C81N3H90Br3	-5.659	-1.768	3.891

whereas the energy gap between HOMO and LUMO is 4.027 eV for the unsubstituted truxene 10.64 The overall band gap between HOMO and LUMO was reduced upon derivatization of the truxene. It was observed that the LUMO level upon derivatization is significantly stabilized compared to that of the unsubstituted truxene core. Noticeably, the HOMO levels of compounds 10 and 17 were found to be more stable than that of other compounds. The greatest stability of the HOMO and LUMO for compound 10 may be due to the presence of the carbonyl functionality in place of the indole moiety at the periphery. It has been reported in the literature that the HOMO and LUMO orbitals of the unsubstituted truxene core are delocalized in nature. Upon derivatization, the HOMO orbitals of the compounds shift to one of the three electronrich peripheral indole arms of the molecules; however, the LUMO orbitals exhibit a greater extent of delocalization. Moreover, it is observed that the HOMO and HOMO - 1 and the LUMO and LUMO + 1 are nearly degenerate for these compounds. It is also found that, apart from HOMO \rightarrow LUMO, the $S_0 \rightarrow S_1$ transition is composed of HOMO \rightarrow LUMO + 1, HOMO - 1 \rightarrow LUMO, and HOMO - 1 \rightarrow LUMO + 1. Similar degenerate HOMOs and LUMOs in trisilatruxene and trioxatruxene have been reported previously.⁴⁶ Detailed information about the various transitions (S_0 \rightarrow S₁) for the present indole functionalized truxene derivatives is provided in the Supporting Information (Figure S2).

Furthermore, time-dependent density functional theory (TD-DFT) calculations were carried out in DCM using the solvation model (SMD) in Gaussian 09 software. The 6-311G/



Figure 4. Comparison of experimental and calculated (TD-DFT at the B3LYP level) UV-vis spectra of indolo-truxene derivatives in DCM solvent.

B3LYP basis set was used for all of the calculations. The TD-DFT predicted vertical excitation energies shown in Figure 4 along with experimental UV–visible (UV–vis) spectra. The calculated λ_{abs} values are in accordance with the experimental value which are listed in Table 4.

Table 4. Experimental and Theoretical Absorption Maxima (λ_{abs}) along with the Oscilator Strength (f) of the Indolo-Truxene Derivatives

compound	λ_{abs} (exp) (nm)	λ_{abs} (theo) (nm)	f (oscilator strength)
10	334	344	0.0176
20	351	358	0.0578
17	350	356	0.1622
24	337	345	0.1813
22	350	355	0.0429
18	335	327	0.0712

3. CONCLUSIONS

In summary, herein we have for the first time prepared several indole-based C_3 -symmetric truxene derivatives by utilizing cyclotrimerization and both 3-fold Friedel–Crafts acylation and Fischer indolization reactions as key steps. The synthesized indolo-truxene derivatives were fully characterized using NMR spectroscopy and mass spectrometry. The photophysical properties of the thus-constructed molecules have been investigated using steady-state absorption and fluorescence and time-resolved fluorescence techniques. Moreover, DFT calculations have been discussed to understand the photophysical properties of the indolo-truxene molecules. These results may open new possibilities to the researchers working in this field.

4. EXPERIMENTAL SECTION

4.1. General Details. All the commercially available reagents were used without further purification and purchased from Sigma-Aldrich, Alfa Aesar, TCI, GLR, Avera and Spectrochem, etc. Solvents were purified according to the standard reported procedures. Analytical thin layer chromatography (TLC) was performed on aluminum plates coated with silica gel by using a suitable mixture of ethyl acetate (EtOAc)

and petroleum ether (PE) as developer. Column chromatography was performed using silica gel (100-200 mesh) with an appropriate mixture of EtOAc and PE. Steady-state absorption measurements of the samples were carried out using an UVvis spectrophotometer (UV-2600i, Shimadzu). Steady-state fluorescence measurements were performed using a fluorimeter (Fluorolog 3, Horiba). Time-resolved fluorescence intensity decays of the samples were measured using a timecorrelated single photon counting instrument (LifeSpec-II, Edinburgh Instruments, Livingston, U.K.) with a LED excitation source of 320 nm and MCP PMT detector. The full width at half maxima (fwhm) of the instrument response function (IRF) was found to be ~800 ps. The fluorescence lifetimes of the samples were obtained by fitting the measured decays with exponential function using iterative reconvolution algorithm.⁶⁵ All spectroscopic measurements have successfully been carried out using a standard quartz cuvette at ~298 K.

4.1.1. Synthesis of 10,15-Dihydro-5H-diindeno[1,2-a:1',2'c]fluorene (1). The truxene scaffold 1 was prepared according to the literature report procedure.⁵⁷ l-Indanone 13 (6.8 g, 51.4 mmol) was added to a mixture of 60 mL of acetic acid and 30 mL of concentrated HCl, and then the reaction mixture was stirred for 16 h at 100 °C. The solid precipitate was obtained by pouring the reaction mixture into the crushed ice; washing with water and acetone followed by dichloromethane offered a creamy solid compound (4.7 g, 80%).

4.1.2. Synthesis of 5,5,10,10,15,15-Hexabutyl-10,15-dihy*dro-5H-diindeno[1,2-a:1',2'-c]fluorene* (14). Truxene 1 (4 g, 11.68 mmol), DMSO (35 mL), and ^tBuOK (11.79 g, 105.12 mmol) were mixed in a two-neck round-bottom flask (100 mL) under a nitrogen atmosphere. The flask was cooled to 0 °C and stirred viciously; after that "BuBr (11.30 mL, 105.12 mmol) was slowly added to the flask, and the stirring was continued for 24 h at room temperature (RT), until the completion of the reaction (TLC monitoring). Then, the reaction mixture was quenched with water and the crude product was extracted with ethyl acetate. The combined organic layer was washed with water (100 mL \times 2) and dried over Na₂SO₄. After evaporation of the solvent, the residue was passed through silica gel (SiO_2) to give the final product as a white powder (7.5 g, 95%). The ¹H NMR spectrum was perfectly matched with the previously reported one.⁵

4.1.3. Synthesis of 1,1',1"-(5,5,10,10,15,15-Hexabutyl-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12triyl)tris(propan-1-one) (10). Compound 14 (2 g, 2.94 mmol) was dissolved in dichloromethane (15 mL). This solution was gradually added to the AlCl₃/propionyl chloride solution at 0 °C, which was prepared by dissolving AlCl₃ (3.53 g, 26.46 mmol) in propionyl chloride 15 (58.8 mmol) at 0 °C under a nitrogen atmosphere. The red reaction mixture was stirred for 30 min at 0 °C and further stirred at room temperature for 6 h. The mixture was poured gradually into the crushed ice cold water (~150 mL) while stirring. The resulting mixture was then stirred at rt for 15 min. Aqueous solution was extracted with CH₂Cl₂, washed with a saturated aqueous NaHCO₃ solution, and dried over Na2SO4. The solvent was removed under reduced pressure to afford the crude product as a paleyellow solid, which was then purified by silica gel column chromatography (15% ethyl acetate and petroleum ether) to give product 10 (2.44 g, 98%) pale-yellow solid; mp: 210-212 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, J = 8 Hz, 3H), 8.10-8.04 (m, 6H), 3.17-3.12 (q, J = 8 Hz, 6H), 3.10-2.93 (m, 6H), 2.23–2.18 (m, 6H), 1.31 (t, J = 8 Hz, 9H), 0.87–0.85 (m, 12H), 0.51–0.40 (m, 30H); ¹³C NMR (101 MHz, CDCl₃) δ 199.55, 152.66, 147.08, 143.13, 136.77, 134.04, 125.77, 123.35, 120.41, 54.90, 35.37, 30.82, 25.38, 21.59, 12.62, 7.27; MS (MALDI): $m/z = 847.068 [M^+]$.

4.2. General Procedure for the Formation of Truxene-Based Indole Derivatives 17, 20, 22, and 24. A solution of compound **10** (1 equiv), phenylhydrazine derivatives (6 equiv), and *p*-toluenesulfonic acid (*p*-TsOH, 6 equiv) in dry EtOH (10 mL) was refluxed for 12 h. At the reaction completion (TLC monitoring), the reaction mixture was then cooled to rt, the EtOH was removed, and the reaction mixture was diluted with water and then organic layer was extracted with DCM. The solvent was removed under reduced pressure, and the crude products were purified by silica gel column chromatography utilizing an appropriate mixture of EtOAc-PE to afford the desired corresponding products.

4.2.1. 2,2',2"-(5,5,10,10,15,15-Hexabutyl-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12-triyl)tris(5-bromo-3-methyl-1H-indole) (17). Gray solid; yield = 67% (412 mg, starting from 400 mg of 13); $R_{\rm f}$ = 0.70 (20% ethyl acetate/ petroleum ether); mp: 154–159 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 8 Hz, 3H), 8.18 (s, 3H), 7.70 (s, 3H), 7.61–7.56 (m, 6H), 7.24 (s, 5H), 7.18 (s, 1H), 3.0–2.94 (m, 6H), 2.48 (s, 9H), 2.16–2.10 (m, 6H), 0.93–0.84 (m, 12H), 0.60–0.41 (m, 30H); ¹³C NMR (101 MHz, CDCl₃) δ 154.26, 145.60, 139.68, 138.13, 135.63, 134.51, 132.04, 130.88, 125.70, 125.07, 121.59, 121.42, 112.80, 112.07, 108.45, 55.85, 36.83, 26.64, 22.90, 13.89, 9.94; MS (MALDI):*m*/*z* = 1300.790 [M⁺].

4.2.2. 2,2',2"-(5,5,10,10,15,15-Hexabutyl-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12-triyl)tris(3-methyl-1H-indole) (**20**). Brown solid; yield = 90% (230 mg, starting from 200 mg of **13**); $R_f = 0.43$ (20% ethyl acetate/petroleum ether); mp: 160–162 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, *J* = 8, 3H), 8.22 (s, 3H), 7.70–7.66 (m, 8H), 7.44 (d, *J* = 8, 3H), 7.26–7.17 (m, 7H), 3.12–3.00 (m, 6H), 2.61 (s, 9H), 2.27–2.15 (m, 6H), 1.03–0.89 (m, 12H), 0.65–0.49 (m, 30H); ¹³C NMR (101 MHz, CDCl₃) δ 154.35, 145.55, 139.54, 138.32, 136.09, 134.54, 131.53, 130.39, 125.75, 125.14, 122.50, 121.56, 119.74, 119.10, 110.79, 109.08, 108.98, 55.94, 36.99, 26.78, 23.07, 14.04, 10.26; MS (MALDI): *m*/*z* = 1066.099 [M⁺]. 4.2.3. 2,2',2"-(5,5,10,10,15,15-Hexabutyl-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12-triyl)tris(5-chloro-3-methyl-1H-indole) (22). Light orange solid; yield = 57% (315 mg, starting from 400 mg of 13); $R_{\rm f}$ = 0.44 (20% ethyl acetate/petroleum ether); mp: 133–135 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, J = 8 Hz, 3H), 8.19 (s, 3H), 7.61– 7.54 (m, 9H), 7.28–7.25 (m, 3H), 7.12–7.10 (m, 3H), 3.02– 2.94 (m, 6H), 2.48 (s, 9H), 2.17–2.09 (m, 6H), 0.93–0.84 (m, 12H), 0.58–0.40 (m, 30H); ¹³C NMR (101 MHz, CDCl₃) δ 153.29, 144.62, 138.70, 137.17, 134.84, 133.27, 130.42, 129.96, 124.72, 124.29, 121.55, 120.44, 117.51, 110.68, 107.56, 54.87, 35.86, 25.67, 21.95, 12.94, 9.00; MS (MALDI): m/z = 1168.536 [M⁺].

4.2.4. 2,2',2"-(5,5,10,10,15,15-Hexabutyl-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12-triyl)tris(1,3-dimethyl-1H-indole) (24). Green solid; yield = 52% (275 mg, starting from 400 mg of 13); $R_{\rm f}$ = 0.76 (20% ethyl acetate/ petroleum ether); mp: 110–112 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.52 (d, *J* = 8 Hz, 3H), 7.69 (d, *J* = 8 Hz, 3H), 7.56 (s, 3H), 7.49 (d, *J* = 8 Hz, 3H), 7.42 (d, *J* = 8 Hz, 3H), 7.34– 7.31 (m, 3H), 7.28–7.22 (m, 3H), 3.78 (s, 9H), 3.11–3.08 (m, 6H), 2.45 (s, 9H), 2.25–2.20 (m, 6H), 1.04–0.99 (m, 12H), 0.71–0.54 (m, 30H); ¹³C NMR (101 MHz, CDCl₃) δ 153.63, 145.62, 139.67, 138.28, 138.06, 137.43, 130.06, 128.61, 124.60, 121.78, 119.19, 118.82, 109.26, 108.63, 55.74, 36.63, 31.16, 26.64, 22.87, 13.87, 9.59; MS (MALDI): m/z = 1107.814 [M⁺].

4.2.5. 2,2',2"-(5,5,10,10,15,15-Hexabutyl-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12-triyl)tris(5-bromo-1,3-dimethyl-1H-indole) (18). NaH (184 mg, 61.38 mmol) was added into the solution of 15 (800 mg, 6.13 mmol) in DMF (10 mL) at 0 °C. The heterogeneous mixture was stirred at 0 °C for 30 min, and then iodomethane (0.38 mL, 61.38 mmol) was added into it. After 12 h, the reaction mixture was cooled to 0 °C and quenched with saturated aq. NH₄Cl. The organic phase was extracted with EtOAc and dried over anhydrous Na2SO4. The product was obtained by column chromatography on silica gel (5% EtOAc/petroleum ether) to give product 18 (718 mg, 87%) pale-yellow solid, yield; $R_{\rm f}$ = 0.43 (10% ethyl acetate/petroleum ether); mp: 130–132 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 7.6 Hz, 3H), 7.69 (s, 3H), 7.44 (s, 3H), 7.37 (d, J = 8 Hz, 3H), 7.28 (d, J = 8 Hz, 3H), 7.17 (d, J = 8 Hz, 3H), 3.65 (s, 9H), 2.99–2.95 (m, 6H), 2.29 (s, 9H), 2.14-2.11 (m, 6H), 0.91-0.81 (m, 12H), 0.58-0.43 (m, 30H); $^{13}\mathrm{C}$ NMR (101 MHz, CDCl₃) δ 152.72, 144.79, 138.91, 138.21, 137.24, 135.08, 129.32, 128.57, 127.48, 124.03, 123.61, 123.54, 123.46, 120.41, 111.43, 109.76, 107.30, 76.36, 54.81, 35.64, 30.33, 25.66, 21.87, 12.90, 8.54; MS (MALDI): $m/z = 1342.439 [M^+]$.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c07770.

Characterization part (¹H NMR, ¹³C NMR, and MALDI) of all the synthesized compounds (PDF)

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Notes

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