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PAPER

Synthesis of electron deficient acene derivatives *via* a bidirectional iterative elongation reaction†

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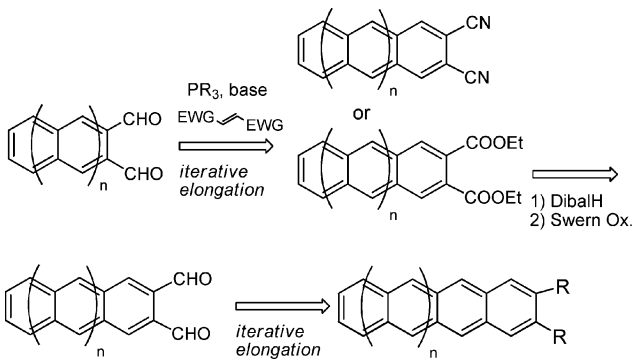
Previously, we developed an iterative elongation methodology to synthesize acene esters, nitriles, and imides. The strategy uses the concept of bidirectional synthesis, and we can now make a series of electron deficient anthracene, tetracene, and pentacene derivatives *via* the bidirectional iterative elongation protocol. Central units, used to initiate the bidirectional elongation, were synthesized by employing a double anionic Fries rearrangement as the key step. The photophysical and electrochemical properties of these novel electron acceptors are investigated and interpreted based on the electron withdrawing power of the substitutions. An excited state charge transfer was proposed for one compound to account for its peculiar fluorescent behavior.

Introduction

In the past two decades, organic semiconductor-based material electronic devices have become a fruitful area for both basic scientific research and practical applications.[1] It is hoped the inexpensive, light, flexible, and processable organic materials might some day work alone or even replace their inorganic counterparts. In this grand pursuit, the role of synthetic organic chemists is to provide the basic building blocks for all subsequent endeavors. With the capacity to generate incremental structural variations through synthetic manipulations, scientist can in principle fine-tune and optimize the material properties. However, this "structural tunability" is purely conjectural unless systematic and efficient synthetic accessibility to a desired class of structure is well established.

Among the types of compounds exploited for organic electronic materials, linearly fused acene is possibly the most versatile.[2] Unfortunately, these aromatic systems are also among the most difficult to synthesize. In more than 3000 pentacene related publications in the last decade, the majority of pentacene derivatives are synthesized by just one method, reductive alkynylation or arylation (R–C≡C–Li/$SnCl_2$ or PhLi/$SnCl_2$) of the corresponding pentaquinones.[3] To further explore the scope and limitation of acene derivatives in various applications, we have developed a convenient iterative synthetic scheme to construct this class of molecule (Scheme 1).[4] A Wittig reaction between [*N*]acene-2,3-dicarbaldehyde and 2-(trialkyl-λ_5-phosphanylidene)-succinic acid diester (generated from dialkyl maleate and trialkyl phosphine)[5] produces 2-(3-formyl-[*N*]acene-2-ylmethylene)-succinic acid diester. DBU was then added to affect an intramolecular Knoevenagel condensation to furnish the [*N*+1] acene-2,3-diethyl diester. The diester thus produced can then be readily converted into another dialdehyde (dibalH reduction and Swern oxidation) to undergo a further round of elongation. [*N*+1] acene-2,3-dinitrile can also be synthesized from the same starting compound if dialkyl maleate was switched to fumaronitrile. Such cyanated acene derivatives have recently attracted considerable interest due to their potential in a variety of applications ranging from N-type semiconductors in field effect transistors to electron acceptors in solar cells.[6]



Scheme 1 Iterative elongation protocol for acene derivatives.

For the synthesis of linear symmetric oligomers like acene molecules, the most intuitive retrosynthesis is the bidirectional elongation from a central unit.[7] This concept has been extensively explored by Takahashi's group *via* zirconocene-mediated cyclotrimerization (Scheme 2a).[8] By combining the two concepts of iterative and bidirectional elongation, we can concoct a greatly effective and simplified protocol for acene synthesis (Scheme 2b). In this article, we wish to report our preliminary results in this pursuit. Since the products of our iterative elongation reaction

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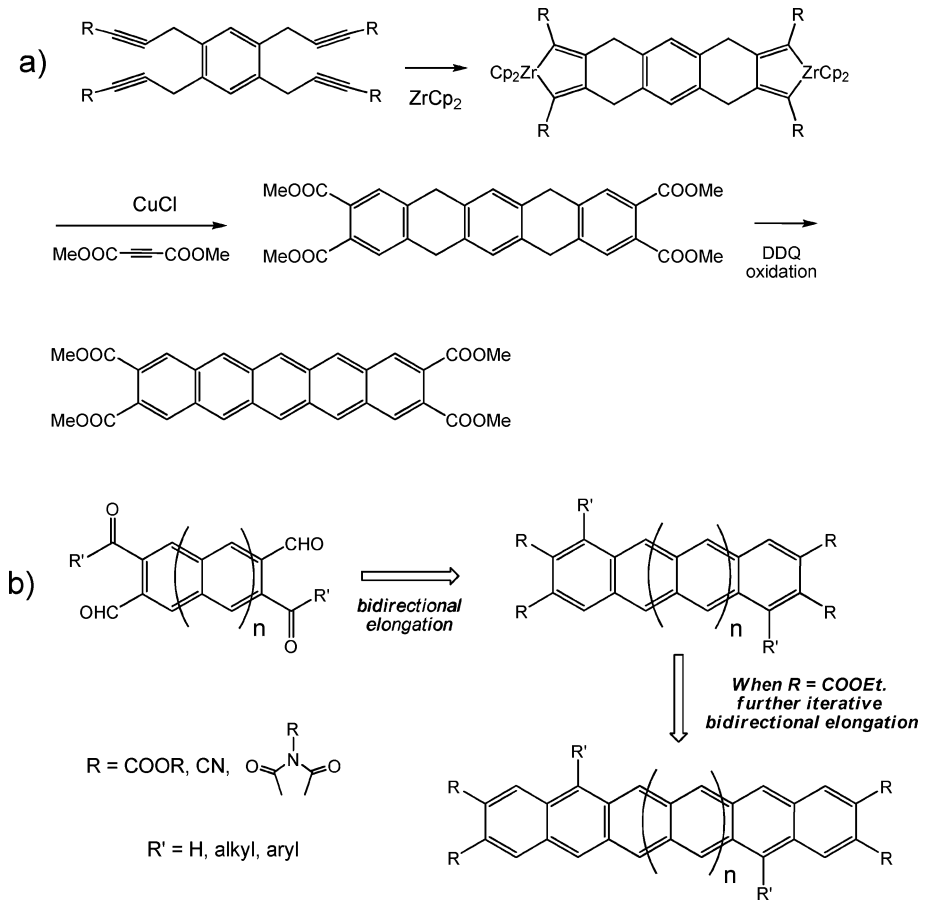


Scheme 2 Bidirectional elongation for acene derivatives based on zirconocene-mediated cyclization and homoelongation.

are invariably carrying ester or nitrile groups, this strategy enables us to access various electron deficient acene derivatives that are hitherto hard to synthesize. In addition, we also wish to report how we extended the scope of the elongation reaction to produce imide products.

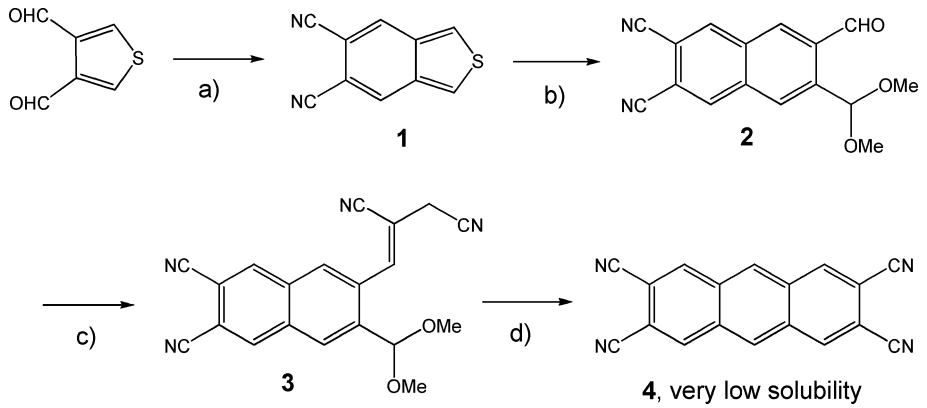
Result and discussion

1. Synthesis

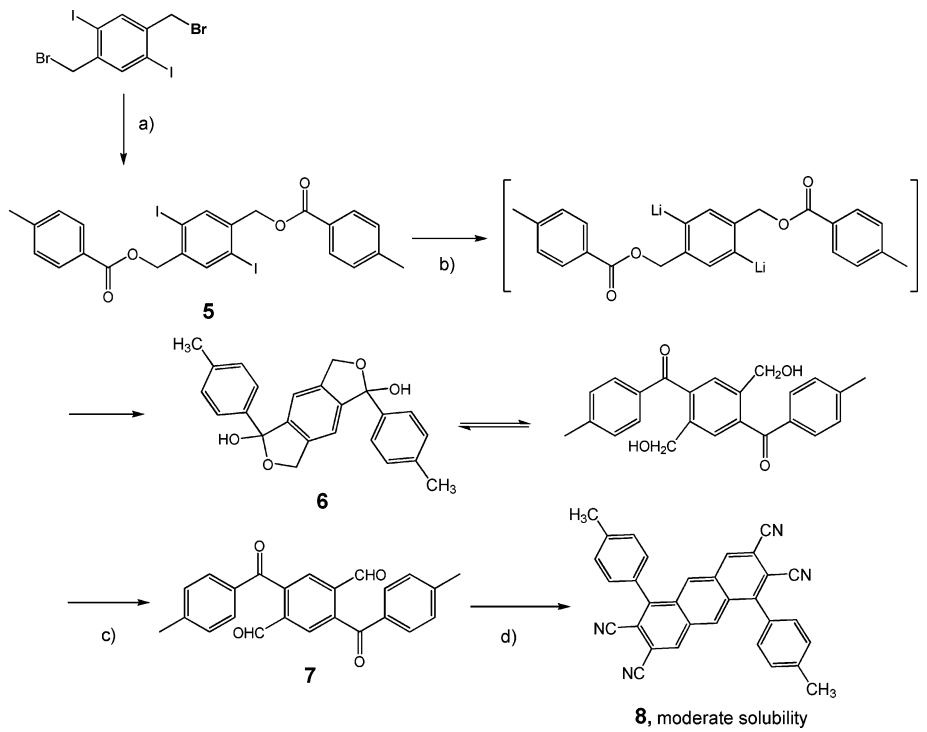
Since a computational study predicted 2,3,6,7-tetracyanoanthracene to be a good electron transporting material,[6a] this seemingly simple compound fittingly became our first target. The most straightforward retrosynthetic analysis is to perform bidirectional elongation with benzene-1,2,4,5-tetracarbaldehyde. However, due to the instability of the tetracarbaldehyde, we devised an alternative two-stage elongation route. As shown in Scheme 3, compound **1**, benzo[*c*]thiophene-5,6-dicarbonitrile, was synthesized from thiophene-3,4-dicarbaldehyde according to a known procedure we previously developed.[9] A Diels–Alder reaction was carried out using this benzo[*c*]thiophene **1** as the diene and 4,4-dimethoxybut-2-ynal[10] as the dienophile to furnish tetra-substituted naphthalene **2**. The aldehyde in **2** was then converted to dicyanopropenyl *via* the Wittig reaction. The dimethylacetal masked aldehyde was then hydrolyzed with formic acid. The subsequent intramolecular Knoevenagel condensation took place spontaneously to give the product **4** in moderate yield. In this scheme, we intentionally split the original elongation reaction into step c and d. This strategic detour is necessary to alleviate solubility problems we encountered in isolating **4** and the unprotected intermediate.

The abysmal solubility of **4** proved to be the major obstacle in its characterization and application of this electron deficient anthracene. The solution phase ^{13}C spectrum can not be obtained even in saturated DMSO solution after 16 000 scans. The solid state ^{13}C spectrum, though feasible, is not informative. Further purification for device application is also problematic. After wrestling with these difficulties, we conceded the necessity to re-design our strategy to incorporate solubilizing groups unto the acene structures.

Through the pioneering studies of Anthony, Nuckolls, and Miller,[11] it is now well established that substitutions at the *peri*-position can effectively solubilize the acene skeleton by disrupting the edge–face interaction. To apply this concept to bidirectional elongation, we need to prepare 1,4-diformy-2,5-diketone benzene derivatives (like compound **7**) on a practical scale as the central unit. To our surprise, synthetic approaches to the crucial *ortho*-ketone benzaldehyde structural motif are quite rare in the literature. After several futile attempts, we finally developed a convenient entry into this class of compounds based on an anionic Fries rearrangement first reported by Rodrigo and latter utilized by Keck and Nicolaou.[12] As shown in Scheme 4,



Scheme 3 Synthesis of 2,3,6,7-tetracyanoamthracene. a) fumaronitrile, triethyl phosphine, DBU, CH_2Cl_2. b) 4,4-Dimethoxybut-2-ynal, toluene, reflux, 58%. c) Fumaronitrile, triethyl phosphine, CH_2Cl_2, room temperature, 57%. d) Formic acid, room temperature, 93%.



Scheme 4 Synthesis of 1,5-ditolyl-2,3,6,7-tetracyanoanthracene *via* bidirectional elongation. a) Toluic acid, K_2CO_3, DMF 79%. b) –114 °C, n-BuLi, THF. c) PDC, CH_2Cl_2. d) PEt_3, fumaronitrile, DBU, 30% over three steps.

starting from the diiodo-dibenzoylxylylene (synthesized from 1,4-bis(bromomethyl)-2,5-diiodobenzene and *p*-toluic acid *via* S_{N2} reaction, see ESI†), we carried out a double lithium-iodine exchange at low temperature (–114 °C). The benzoyl groups then underwent intramolecular transfer to give the bis-lactol **6**. Since the lactol is in equilibrium with the open form keto-alcohol, such compounds can be readily oxidized by PDC or PCC to furnish the desired 2,5-bis(4-methylbenzoyl)terephthalaldehyde in moderate yield. It should be noted that substantial portion of compound **6** and **7** decomposed when purifications were attempted using flash chromatography. It is therefore recommended that both compounds be used in the subsequent steps without further purification. Fortunately, the final bidirectional elongation reaction can be performed with crude **7** to produce target 1,5-ditoyl-2,3,6,7-tetracyanoanthacene (**8**). Although the overall yield over three steps (**5–8**) is only around 30%, this reaction sequence is nonetheless efficient since it includes six carbon–carbon bond formation steps (two C–C bonds formed in **5–6** and four in **7–8**) and a double oxidation (**6–7**). As anticipated, the solubility of **8** (0.67 mg mL^{-1} in CH_2Cl_2) is indeed much improved compared to **4**. Single crystals suitable for structural analysis can be grown from a saturated acetonitrile solution. As shown in the ORTEP structure (Fig. 1), the anthracene skeleton is planar. The dihedral angle between tolyl groups and anthracene is 64.5°. The anthracene skeleton forms π–π dimers with 0.34 nm face-to-face distance in the solid state. The nearest center-to-center distance between the dimers is measured as 0.78 nm.

Our strategy provides an opportunity to selectively construct electron deficient acene derivatives bearing different substitution patterns. As shown in Scheme 5, when the starting

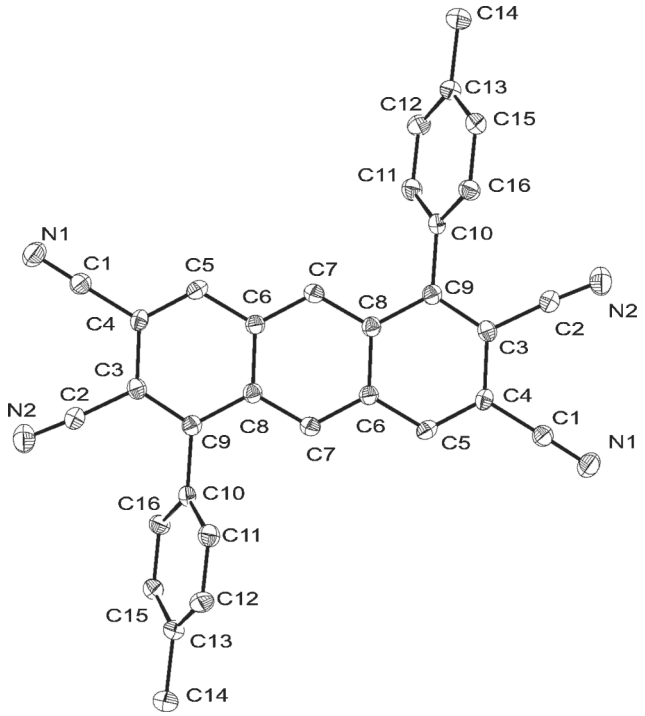


Fig. 1 ORTEP picture of anthracene tetranitrile **8**.

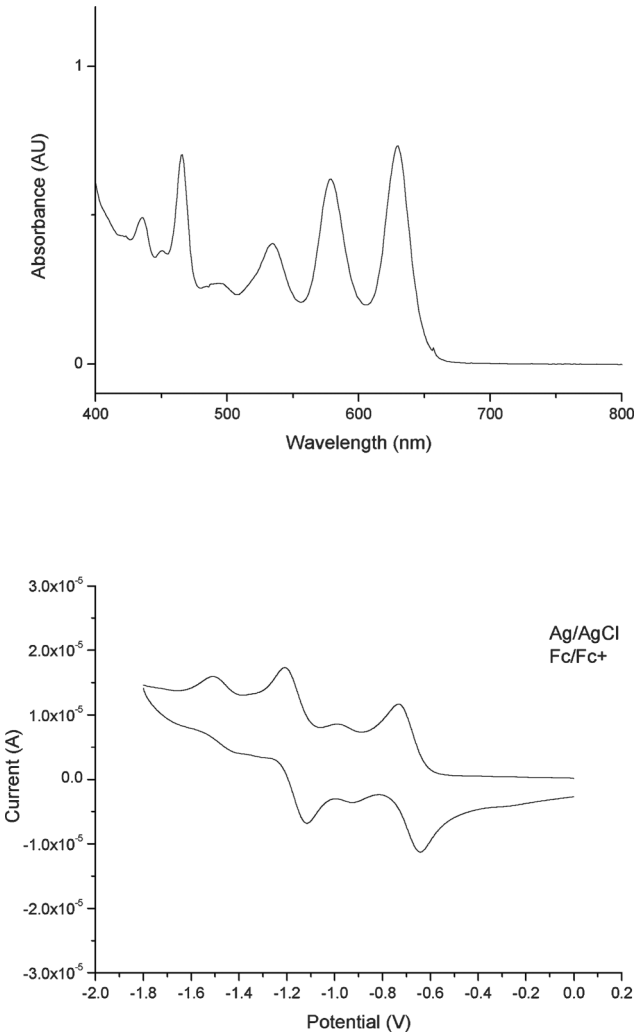
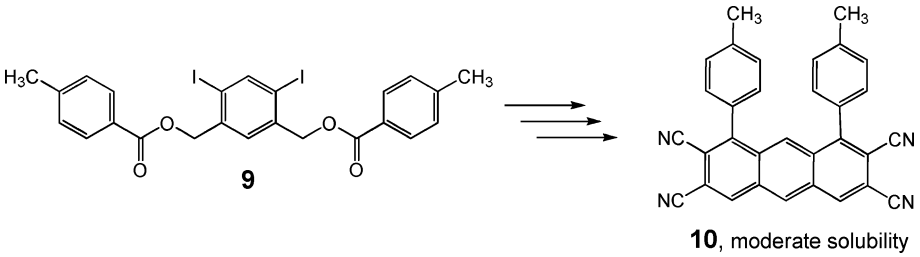


Fig. 2 UV spectrum and CV curve of pentacene tetranitrile **17**.

1,4-diiodo-2,5-diester xylylene in Scheme 4 was switched to 1,3-diiodo-4,6-diester isomer (**9**), we can accordingly obtain 1,8-ditolyl-2,3,6,7-tetracyanoanthracene (**10**) in comparable yield following the identical three-step procedure. The 1,5-ditolyl isomer **8** possesses C_{2h} symmetry while the 1,8-isomer C_{2v}. This difference in molecular shape should induce distinct solid state arrangement in the two compounds. We hope such a substitution effect can be further exploited to control crystal packing and electronic properties in real devices.

Although both **8** and **10** are moderately soluble (0.67 and 2.5 mg mL^{-1} in CH_2Cl_2 respectively), their ^{13}C spectrums are still hardly attainable in saturated $CDCl_3$ solutions. Clearly, if we are to further employ the bidirectional approach to synthesize tetracene and pentacene derivatives, more solvophilic groups must be attached to the acene backbone. With the established strategy in Scheme 4 and 5, this can be easily accomplished by starting with diiodo-dibenzoate benzene carrying four alkyl groups as compound **11**. The compound was duly converted to 2,5-bisbenzoyl terephthalaldehyde **12** after benzoyl transfer and PDC oxidation. The bidirectional elongation using fumaronitrile and diethyl maleate gave tetranitrile **13** and tetraester **15** respectively. The solubility of **13** dramatically improves to 120 mg mL^{-1}, adequate for almost any further synthetic manipulation.

On surveying the literature, imide is another very common electron withdrawing substitution found on *N*-type organic materials. Notable examples include various perylene and rylene diimide,[13] and anthracene diimide.[14] We believe, with slight modification, our original homoelongation strategy can also produce this class of electron acceptor. A model study was first carried out. *N*-alkylmaleimide was first treated with triethyl phosphine to produce a cyclic ylide which then underwent a Wittig reaction with phthalaldehyde. DBU was then added to induce the intramolecular

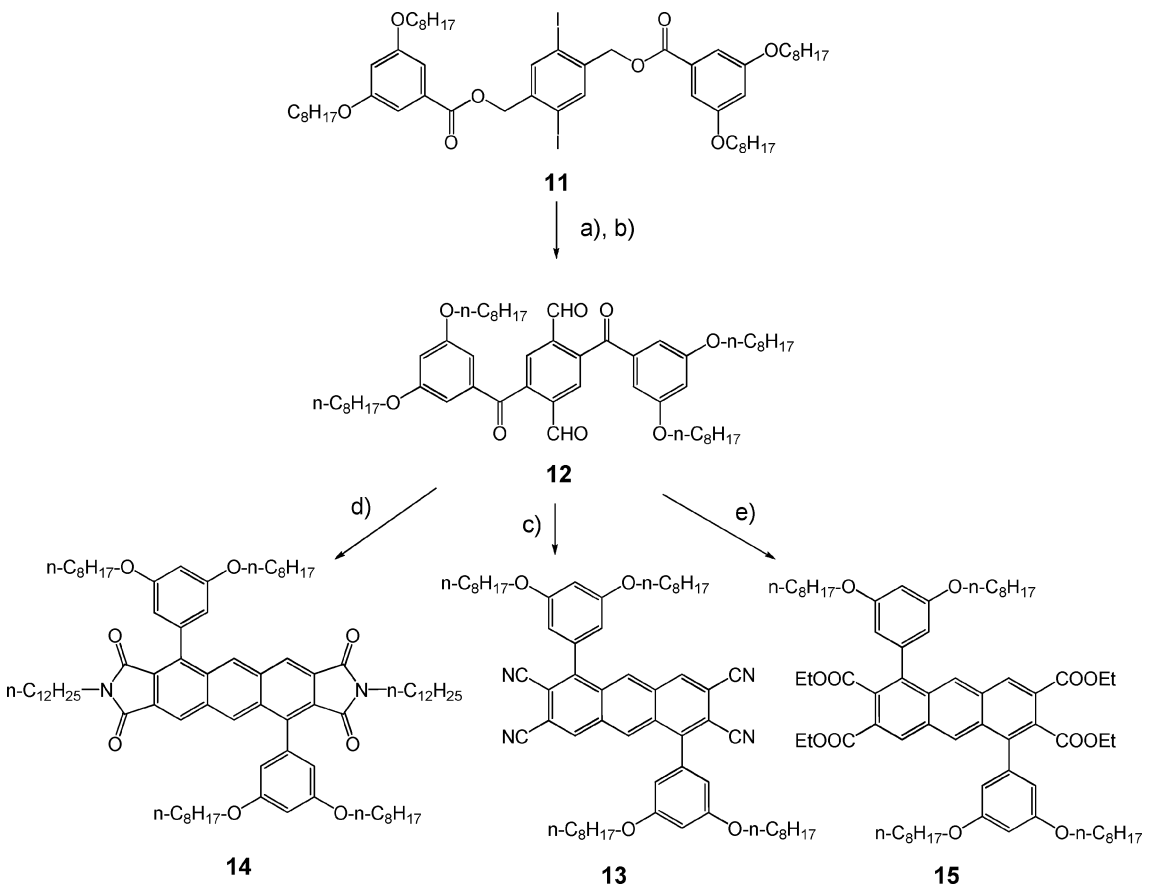


Scheme 5 Synthesis of 1,8-ditolyl-2,3,6,7-tetracyanoanthracene *via* bidirectional elongation.

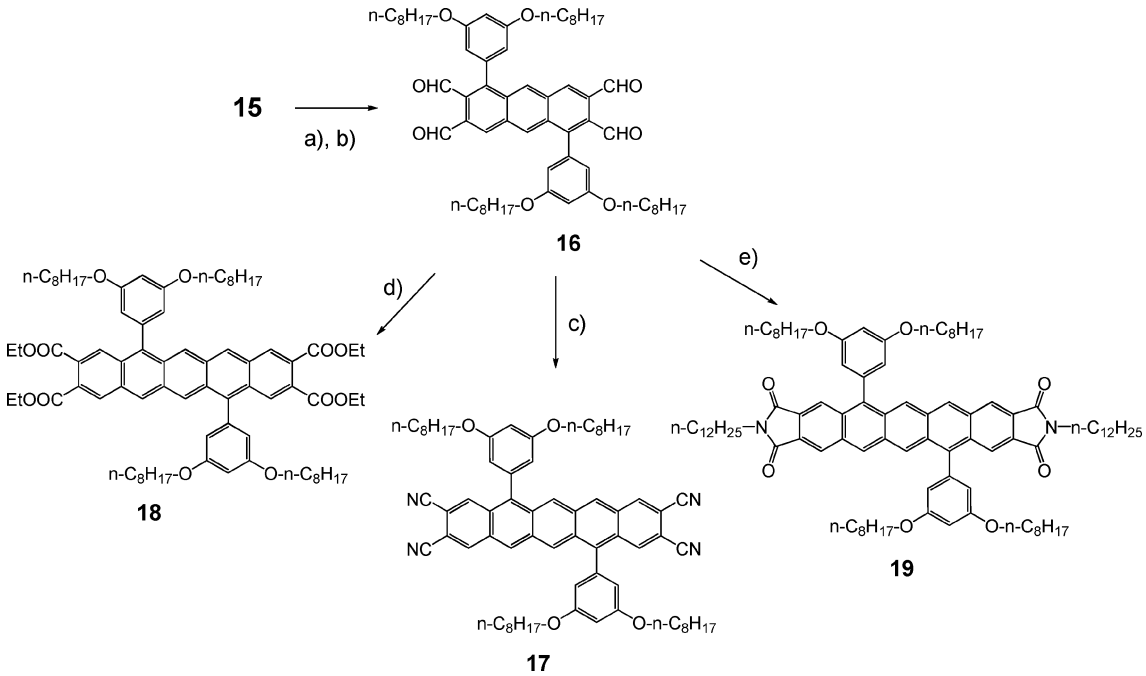
Knonevanegal condensation to deliver the naphthalene imide product. When **12** was subjected to this newly developed reaction condition, anthracene diimide **14**, the bidirectional elongation product, was produced in good yield. As depicted in Scheme 6, we now have three distinctive elongation conditions at our disposal to produce acene diesters, nitrile, and imide respectively. These protocols will be employed in the further synthesis of tetracene and pentacene derivatives.

Since the original elongation strategy is an iterative reaction sequence, this concept can be united with bidirectional approach to make higher acene derivatives. The consummation of these two ideas is shown in Scheme 7. The anthracene tetraester **15** was transformed to tetraldehyde **16** in two redox steps. Compound **16** can then undergo a bidirectional elongation reaction with fumaronitrile, diethyl maleate, or *N*-n-dodecyl-maleimide to produce pentacene tetranitrile **17**, tetraester **18**, and diimide **19** respectively. The yields over this three step reaction sequence are moderate (17–57%). Nevertheless, we consider such efficiency satisfactory considering a total of 16 transformations (four reductions, four oxidations, eight C–C bond formations) take place on relatively sensitive substrates during these three steps. All three compounds are highly soluble in common organic solvents. Due to the presence of multiple electron withdrawing substitutions, these pentacene derivatives are more resistant to oxidative decomposition than those also unsubstituted at the 5 and 13 carbon. All three compounds are stable in the solid state for at least six months. More remarkably, the $CDCl_3$ solution of tetranitrile **17** can be stored in the dark under ambient conditions for 18 h without noticeable decomposition. Even under ambient conditions, the half life of **17** solution is about 60 min, nearly 20 times superior to similar compounds without the electron withdrawing groups.[11d] This observation indicates that attaching electron withdrawing substitutions, especially nitrile, to an acene backbone can provide an alternative approach to stabilize acene structures. In addition, the strategy is the first reaction sequence to produce pentacene derivatives with C_{2h} symmetry. With new substitution patterns, novel crystal packing motifs and therefore improved electronic properties might emerge in these systems.

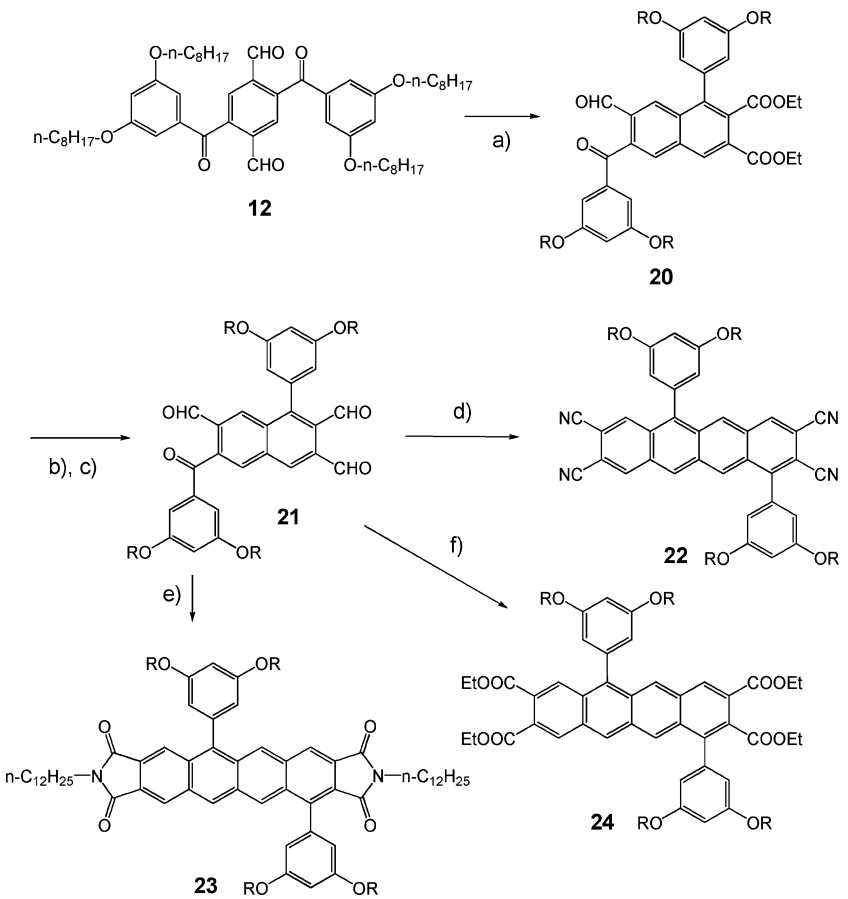
The synthesis of tetracene derivatives *via* bidirectional approach is less straightforward since the central unit to launch the elongation must be a naphthalene derivative. Nevertheless, we have worked out a scheme that combines both unidirectional and bidirectional elongation to furnish such electron deficient tetracene derivatives. As shown in Scheme 8, **12** first underwent unidirectional elongation to give the naphthalene diester **20**. All four carbonyl groups in **20** were then reduced to alcohol with $LiBH_4$. The tetraol thus produced was then converted to trialdehyde **21** using Swern oxidation. **21** can then undergo bidirectional elongation to give tetranitrile **22**, diimide **23**, and tetraester **24**.



Scheme 6 Synthesis of solubilized anthracene with electron withdrawing functional groups *via* bidirectional elongation. a) –114 °C, n-BuLi, THF. b) PDC, CH_2Cl_2. c) PEt_3, fumryl nitrile, DBU, CH_2Cl_2, 29% over three steps. d) PEt_3, 1-dodecyl-1*H*-pyrrole-2,5-dione, DBU, CH_2Cl_2, 35% over three steps. e) PEt_3, diethyl maleate, DBU, CH_2Cl_2, 32% over three steps.



Scheme 7 Synthesis of pentacene tetranitrile, pentacene tetraester, pentacene diimide *via* bidirectional elongation. a) $LiBH_4$, $B(OMe)_3$, THF. b) $(COCl)_2$, DMSO, CH_2Cl_2, −78 °C, Et_3N. c) PEt_3, fumryl nitrile, DBU, CH_2Cl_2, 19% over three steps. d) PEt_3, diethyl maleate, DBU, CH_2Cl_2, 17% over three steps. e) PEt_3, 1-dodecyl-1*H*-pyrrole-2,5-dione, DBU, CH_2Cl_2, 57% over three steps.



Scheme 8 Synthesis of tetracene tetranitrile, tetracene tetraester, and tetracene diimide *via* bidirectional elongation. a) One equivalent of PEt_3 and diethyl maleate, DBU, CH_2Cl_2, 52%. b) $LiBH_4$, $B(OMe)_3$, THF. c) $(COCl)_2$, DMSO, CH_2Cl_2, −78 °C, Et_3N. d) PEt_3, fumaronitrile, DBU, CH_2Cl_2, 52% over three steps. e) PEt_3, 1-dodecyl-1*H*-pyrrole-2,5-dione, DBU, CH_2Cl_2, 19% over three steps. f) PEt_3, diethyl maleate, DBU, CH_2Cl_2, 23% over three steps.

Table 1 The photophysical and electrochemical properties of acene derivatives synthesized in the present report

	UV λ_{max}/nm (band gap in eV)	PL λ_{max}/nm (quantum yield)	E_{red}1,2, (LUMO)	HOMO
4	403 (3.00)	416 (9%)	–1.13, –1.42, (–3.57)	–6.57
8	407 (2.84)	464 (29%)	–0.80, –1.41, (–3.42)	–6.26
10	408 (2.84)	465 (19%)	–0.80, –1.13, (–3.42)	–6.26
13	408 (2.80)	570 (0.6%)	–0.91, –1.55, (–3.40)	–6.2
14	425 (2.84)	465 (0.9%)	–1.26, –1.61, (–3.05)	–5.89
15	415 (2.86)	459 (45%)	–1.41, –1.83, (–2.90)	–5.76
17	630 (1.91)	648	–0.69, –1.17, (–3.62)	–5.53
18	611 (1.93)	637	–1.05, –1.46, (–3.28)	–5.21
19	611 (1.95)	640	–0.92, –1.34, (–3.39)	–5.34
22	516 (2.32)	570 (20%)	–0.78, –1.33, (–3.53)	–5.85
23	508 (2.35)	561 (42%)	–1.08, –1.52, (–3.23)	–5.58
24	506 (2.35)	560 (45%)	–1.20, –1.61, (–3.11)	–5.46
[60]PCMB[15]			–1.06,–1.45	
PDI[16]			–0.55	

2. Photochemical and electrochemical studies

The photophysical and electrochemical properties of the synthetic acene derivatives are listed in Table 1. All absorption spectrum exhibit 30–50 nm bathochromic shifts compared to their respective parent acene compounds. Since the λ_{max} values of **4**, **8**, **10**, **13** are very similar, it seems that the phenyl solubilizing groups do not significantly alter the band gap in tetranitrile compounds. Among anthracene derivatives, nitrile substituted **13** possesses a smaller bathochromic shift than diimide **14** and tetraester **15**. However, this trend is curiously reversed in tetrancene (**22**, **23**, **24**) and pentacene (**17**, **18**, **19**) derivatives. We believe this peculiarity is induced by the conformational effect. Due to the steric interaction between the phenyl and ester (or imide) substitutions, the anthracene π-skeleton in **14** and **15** can be slightly distorted to produce the observed red shifts. On the other hand, such steric interaction is unimportant in **13** because of the smaller size of the nitrile group. The tetracene and pentacene compounds are also less affected by this interaction since the phenyl groups and the bulky substitutions are not in proximity to each other.

In general, the fluorescence spectrum data in Table 1 follow the trends observed in other acene derivatives. The Stoke's shifts are moderate (20–50 nm). The quantum yields of anthracene and tetracene derivatives are generally higher than those of pentacene derivatives. The most notable exception among this normality is the tetranitrile anthracene **13**. In contrast to structurally similar compounds **8**, **10** which fluoresce around 460 nm with quantum efficiency near 20%, the fluorescence λ_{max} of **13** is at 570 nm with a much diminished quantum efficiency (0.6%). The most intuitive rationale for this irregularity is that the Frank–Condon state of **13** decays to a weakly fluorescing charge separation state with positive charge delocalized to the dialkoxyl phenyl groups. This exit channel might not be available for **8** and **10** because the positive charge can not be effectively stabilized on the tolyl substitutions. This primitive model, however, fails to explain why tetraccene tetranitrile **22**, though possessing an even lower LUMO than **13**, remains a decent emitter with average Stoke's shift. We believe the apparently conflicting results can only be rationalized in light of more subtle excited state dynamics. Further photophysical and theoretical studies will be conducted to explain this discrepancy. It is tempting to interpret the low fluorescent quantum yield of **14** based on similar charge transfer interaction. However, the small Stoke's shift of **14** is not consistent with this model. Furthermore, a very similar anthracene diimide compound is known to have relatively low fluorescent efficiency (5%).[14b] Therefore, this low emission quantum yield is appropriately considered inherent to the anthracene diimide structure.

The LUMO levels of these compounds are probed by cyclic voltammetry (Table 1). All compounds exhibit two reversible or quasi-reversible redox waves. The qualitative interpretation of these electrochemical results is relatively straightforward. The nitrile substitution clearly exerts the strongest stabilization on the LUMO of all acene compounds. As anticipated, the electron withdrawing effect of the imide group is inferior to that of nitrile but superior to esters. The first reductive wave of tetranitrile pentacene **17** is at 0.69 eV. To the best of our knowledge, this compound is the most electron deficient pentacene derivative yet reported. Two common organic acceptors, [60]PCMB and PDI, are also listed for comparison. The tetranitrile acene derivatives (**8**, **10**, **13**, **17**, **22**) are clearly stronger acceptors then the fullerene based [60]PCMB while still inferior to perylene diimide. From the optical band gap and LUMO energy level data, we can further deduce that the HOMO orbitals are also substantially stabilized by these electron withdrawing groups.

Conclusion

In summary, we have synthesized a series of soluble electron deficient acene derivatives *via* a bidirectional iterative elongation strategy. This newly developed methodology might provide entry into higher acenes beyond pentacene. Due to the presence of electron-withdrawing ester, nitrile, and imide functional groups, both HOMO and LUMO orbitals are stabilized. Moderate bathochromic shifts are also observed in all compounds compared to their parent systems. The fluorescent spectrum of **13** exhibits a uniquely large Stoke's shift and low quantum yield which indicates excited state charge transfer behavior. Some of these compounds have good potential as building blocks in various optical and electronic devices. All these challenges and opportunities are currently being exploited in our group.

Experimental

General procedure A: Lithium-halogen exchange initiated benzoyl transfer

To a cooled (–114 °C, obtained by liquid nitrogen cooled ethanol) THF solution of diiodo-diester compound (*ca.* 0.9 mmol/10 mL

THF) was slowly added *n*-BuLi (3.2 eq) along the wall of the flask. The mixture was stirred and gradually warmed up to ambient temperature in 2–3 h before being stirred for an additional 30 min. The reaction was quenched with saturated NH_4Cl before THF was removed by evaporation. The mixture was then extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$ and concentrated to give the intermediate bis-lactol. A sample suitable for a ^{13}C spectrum can be purified with a short flash column. However, due to their instability, such compounds are used in the next step without further purification.

General procedure B: Oxidation of lactol

Pyridinium dichromate (6 eq) was added to the CH_2Cl_2 solution of bis-lactol (*ca.* 1.3 mmol/10 mL CH_2Cl_2) and the reaction was stirred overnight. Diethyl ether was added to the reaction and the precipitate was removed by passing the solution through a pad of celite. The solvent was evaporated to give the intermediate dialdehyde. A sample suitable for a ^{13}C spectrum can be purified with a short flash column. However, due to their instability, such compounds are used in the next step without further purification.

General procedure C: Elongation to give acene dinitrile, diester, or imide

To a CH_2Cl_2 solution of fumaronitrile (3 eq, *ca.* 2.5 mmol/10 mL CH_2Cl_2) was slowly added triethylphosphine (3 eq, 1.0 M in THF) and the mixed solution was stirred at room temperature for 30 min. The reagent thus generated was then slowly added to a CH_2Cl_2 solution of dialdehyde or *ortho*-ketoaldehyde (*ca.* 0.5 mmol/10 mL CH_2Cl_2). After the reaction was stirred for 2 h, DBU (0.1 eq) was added and the reaction was stirred overnight at room temperature. The solvent was then removed *in vacuo* and the crude product was purified by flash chromatography to give the tetracyano product. Similar procedures were also employed using diethyl maleate or *N*-dodecyl-maleimide in place of fumaronitrile.

General procedure D: Reduction of ester to alcohol

To an ice-cooled THF solution of tetraester and trimethyl borate was slowly added lithium borohydride (8 eq, 2.0 M in THF). After being stirred for 48 h at 40 °C, the reaction was quenched with saturated NH_4Cl. THF was removed by evaporation before the crude product was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and concentrated to give the intermediate alcohols.

General procedure E: Swern oxidation to give *ortho*-dialdehyde

To a cooled CH_2Cl_2 solution of oxalyl chloride (10 eq, −78 °C, oxalyl chloride/CH_2Cl_2 = 1/5) was slowly added a CH_2Cl_2 solution of DMSO (20 eq, DMSO/CH_2Cl_2 = 1/2) and the mixed solution was stirred at low temperature for 15 min. To this chilled solution was then slowly added a DMSO/CH_2Cl_2 (1/2) mixed solution of alcohols (*ca.* 0.2 g/5 mL). Triethylamine (30 eq) was slowly added after the reaction proceeded for 5 h. The reaction was then warmed back to room temperature in 20 min. The solvents were removed *in vacuo* and the residual was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and concentrated to give the aldehyde. Due to their instability, dialdehyde compounds are usually used in the next elongation step without further purification.

2, 6-(dimethoxymethyl)-7-formylnaphthalene-2,3-dicarbonitrile: A toluene (2 mL) solution of 5,6-dicyanobenzo[*c*]-thiophene8 (330 mg), BHT (10 mg) and 4,4-dimethoxybut-2-ynal (2 ml) was refluxed for 5 h in a sealed tube. The crude mixture was then concentrated under vacuum and purified by flash chromatography (CH_2Cl_2–hexane = 2/1 and 1% Et_3N) to give the pure product (290 mg, 58%). IR (KBr) ν/cm^{-1}: 938, 1073, 1099, 1453, 1693, 2230, 2836, 2943; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.44 (s, 6H), 5.97 (s, 1H), 8.24 (s, 1H), 8.40(s, 1H), 8.47 (s, 1H), 8.50 (s, 1H), 10.53 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 54.29, 101.49, 111.69, 112.85, 115.18, 115.24, 127.95, 131.86, 132.45, 134.55, 135.74, 135.88, 136.83, 140.11, 190.61; HRMS. (EI, M^+), $C_{16}H_{12}O_3N_2$, Calc: 280.0848, Found: 280.0851.

3, 6-(2,3-dicyanoprop-1-enyl)-7-(dimethoxymethyl)naphthalene-2,3-dicarbonitrile: To a CH_2Cl_2 (5 mL) solution of fumaronitrile (1.3 eq., 69 mg) was slowly added triethylphosphine (1.3 eq, 1.0 M in THF, 0.88 mL) and the mixed solution was stirred at room temperature for 30 min. The reagent thus generated was then slowly added to a CH_2Cl_2 solution of **2** (190 mg in 10 mL) and the reaction was stirred overnight at room temperature. The crude mixture was concentrated under vacuum and purified by flash chromatography (CH_2Cl_2–hexane = 2/1) to give the mixture products (*E*+*Z*, 130 mg, 57%). IR (KBr) ν/cm^{-1}: 936, 990, 1061, 1079, 1098, 1348, 2235, 2937; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.36 (s, 6H), 3.37 (s, 6H), 3.59 (s, 2H), 3.60 (s, 2H), 5.40 (s, 1H), 5.48 (s, 1H), 7.79 (s, 1H), 7.92(s, 1H), 8.00 (s, 1H), 8.17 (s, 1H), 8.20 (s, 1H), 8.31 (s, 1H), 8.37 (s, 1H), 8.38 (s, 1H), 8.39 (s, 1H), 8.41 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 53.52, 53.76, 101.66, 104.89, 106.91, 111.69, 111.97, 112.18, 114.02, 114.24, 115.12, 115.25, 115.37, 115.69, 116.85, 128.03, 128.28, 128.80, 129.19, 132.43, 132.65, 132.85, 133.03, 133.57, 133.88, 135.51, 135.76, 135.84, 138.76, 138.94, 144.95, 146.93; HRMS. (EI, M^+), $C_{20}H_{14}O_2N_4$, Calc: 342.1117, Found: 342.1112.

4, anthracene-2,3,6,7-tetracarbonitrile: To a CH_2Cl_2 solution of **3** (120 mg in 5 mL) was slowly added formic acid (5 mL) and the mixed solution was stirred at room temperature for 3 h. The reaction was then quenched with saturated $NaHCO_3$, extracted with CH_2Cl_2. After the combined CH_2Cl_2 solution was concentrated *in vacuo*, the solid residue was washed by diethyl ether to give pure product (90 mg, 93%). IR (KBr) ν/cm^{-1}: 794, 938, 1228, 1260, 1410, 1699, 2238, 2923; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.09 (s, 2H), 9.23 (s, 4H); ^{13}C spectrum can not be obtained due to low solubility; HRMS. (EI, M^+), $C_{18}H_6N_4$, Calc: 278.0592, Found: 278.0568.

6, 1,5-di-*p*-tolyl-1,3,5,7-tetrahydroisobenzofuro[5,6-*c*]furan-1,5-diol: The synthesis of bislactol compound **6** was carried out according to general procedure A using diester **5** as the starting compound. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 6H), 4.56–4.80 (m, 4H), 7.30 (d, J = 8.0 Hz, 4H), 7.60 (s, 2H), 7.75 (d, J = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.79, 63.48, 129.43, 130.73, 131.73, 134.27, 140.22, 140.29, 145.04, 197.84.

7, 2,5-bis(4-methylbenzoyl)terephthalaldehyde: The synthesis of crude dialdehyde was carried out according to general procedure B. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 6H), 7.31 (d, J = 8.0 Hz, 4H), 7.72 (d, J = 8.0 Hz, 4H), 8.13 (s, 2H), 10.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.80, 129.70, 129.79, 130.28, 133.66, 137.90, 143.20, 145.72, 189.01, 194.09.

8, 1,5-di-*p*-tolylanthracene-2,3,6,7-tetracarbonitrile: The synthesis of compound **8** was carried out according to general procedure C and the crude mixture was purified by flash chromatography (CH_2Cl_2–hexane = 6/1) to give the product (overall yield from **5** = 30%). IR (KBr) ν/cm^{-1}: 830, 932, 1024, 1364, 1507, 1764, 2227, 2923; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.53 (s, 6H), 7.37 (d, J = 8.0 Hz, 4H), 7.46 (d, J = 8.0 Hz, 4H), 8.44 (s, 2H), 8.50 (s, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 30.29, 111.49, 111.90, 115.93, 116.37, 130.29, 130.56, 131.06, 131.88, 132.62, 132.81, 137.42, 141.37, 150.71; HRMS. (EI, M$^+$), $C_{32}H_{18}N_4$, Calc: 458.1531, Found: 458.1530.

9′, 1,7-di-*p*-tolyl-1,3,5,7-tetrahydroisobenzofuro[5,6-*c*]furan-1,7-diol: The synthesis of this bislactol compound was carried out according to general procedure A using diester **9** as the starting material. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.39 (s, 6H), 4.65 (broad s, 4H), 7.22 (d, J = 8.5 Hz, 4H), 7.47 (s, 1H), 7.65 (d, J = 8.5 Hz, 4H), 7.76 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.68, 63.25, 129.27, 130.56, 131.03, 131.10, 134.28, 135.98, 144.44, 144.85, 197.46.

9″, 4,6-bis(4-methylbenzoyl)isophthalaldehyde: The synthesis of crude dialdehyde **9″** was carried out according to general procedure B from **9′**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 6H), 7.26 (d, J = 8.0 Hz, 4H), 7.56 (s, 1H), 7.66 (d, J = 8.0 Hz, 4H), 8.62 (s, 2H), 10.09 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.76, 128.61, 129.65, 130.05, 131.35, 133.51, 136.09, 145.50, 145.72, 188.77, 194.17.

10, 1,8-di-*p*-tolylanthracene-2,3,6,7-tetracarbonitrile: The synthesis of compound **10** was carried out according to general procedure C from **9″** and the crude mixture was purified by flash chromatography (CH_2Cl_2–hexane = 6/1) to give the product (overall yield from **9** over three steps = 41%). IR (KBr) ν/cm^{-1}: 820, 929, 1361, 1509, 2230, 2924, 3055; ^{1}H NMR (500 MHz, acetone-d_6): δ 2.45 (s, 6H), 7.36 (d, J = 8.0 Hz, 4H), 7.39 (d, J = 8.0 Hz, 4H), 8.22 (s, 1H), 9.07 (s, 2H), 9.21 (s, 1H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 21.65, 110.70, 112.31, 115.97, 116.44, 130.04, 130.19, 130.87, 131.30, 131.56, 132.42, 132.78, 136.71, 140.92, 151.16; HRMS. (EI, M$^+$), $C_{32}H_{18}N_4$, Calc: 458.1531, Found: 458.1526.

11′, (2,5-bis(hydroxymethyl)-1,4-phenylene)bis((3,5-bis-(octyloxy)phenyl)-methanone): Starting from diester **11**, the synthesis of crude compound **11′** was carried out according to general procedure A. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86 (t, J = 6.5 Hz, 12H), 1.23–1.30 (m, 32H), 1.39–1.43 (m, 8H), 1.73–1.79 (m, 8H), 3.14(t, J = 6.5 Hz, 2H), 3.95 (t, J = 6.5 Hz, 8H), 4.59 (d, J = 6.5 Hz, 4H), 6.70 (t, J = 2.0 Hz, 2H), 6.90 (d, J = 2.0 Hz, 4H), 7.61 (s, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 14.45, 23.26, 26.58, 29.75, 29.83, 29.93, 32.42, 63.67, 69.15, 107.17, 109.23, 131.54, 139.48, 140.63, 140.79, 161.02, 198.39.

12, 2,5-bis(3,5-bis(octyloxy)benzoyl)terephthalaldehyde: Starting from **11′**, the synthesis of crude dialdehyde **12** was carried out according to general procedure B. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 12H), 1.27–1.32 (m, 32H), 1.42–1.44 (m, 8H), 1.73–1.79 (m, 8H), 3.97 (t, J = 6.4 Hz, 8H), 6.72 (t, J = 2.4 Hz, 2H), 6.89 (d, J = 2.4 Hz, 4H), 8.14 (s, 2H), 10.08 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.03, 22.60, 25.96, 29.09, 29.17, 29.28, 31.76, 68.51, 107.34, 108.39, 129.84, 137.90, 143.09, 160.62, 188.81, 194.42.

13, 1,5-bis(3,5-bis(octyloxy)phenyl)anthracene-2,3,6,7-tetracarbonitrile: The synthesis of tetranitrile **13** was carried out according to general procedure C from **12** and the crude mixture was purified by flash chromatography (CH_2Cl_2–hexane = 1/1) to give the product (overall yield from **12** over three steps = 29%). IR (KBr) ν/cm^{-1}: 1056, 1177, 1370, 1444, 1466, 2230, 2856, 2926; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, J = 6.8 Hz, 12H), 1.23–1.31 (m, 32H), 1.41–1.47 (m, 8H), 1.53–1.83 (m, 8H), 3.96–4.01 (m, 8H), 6.53 (d, J = 2.0 Hz, 4H), 6.69 (t, J = 2.0 Hz, 4H), 8.47 (s, 2H), 8.54 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.03, 22.59, 25.98, 29.14, 29.16, 29.30, 31.74, 68.44, 102.22, 108.28, 110.70, 111.34, 114.72, 115.39, 130.32, 131.75, 131.91, 135.41, 136.80, 149.97, 160.84; HRMS. (FAB, [M+H]$^+$), $C_{62}H_{79}N_4O_4$, Calc: 943.6101, Found: 943.6107.

14, *N*,*N′*-bis-n-docecyl-1,5-bis(3,5-bis(octyloxy)phenyl)-anthracene-2,3,6,7-bisimide: Starting from **12**, the synthesis of diimide **14** was carried out according to general procedure C. *N*-n-dodecyl-maleimide (3 eq) was used instead of fumaronitrile. The crude mixture was purified by flash chromatography (CH_2Cl_2–hexane = 2/3) to give the pure product (overall yield over three steps from **11** = 35%). IR (KBr) ν/cm^{-1}: 1018, 1176, 1364, 1394, 1592, 1710, 2853, 2924; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80–0.95 (m, 18H), 1.21–1.30 (m, 68H), 1.42–1.44(m, 12H), 1.64–1.82 (m, 16H), 3.65 (t, J = 7.2 Hz, 4H), 3.97 (t, J = 6.8 Hz, 8H), 6.54 (d, J = 2.0 Hz, 4H), 6.66 (t, J = 2.0 Hz, 2H), 8.41 (s, 2H), 8.61 (s, 2H);^{13}C NMR (125 MHz, $CDCl_3$): δ 10.89, 14.01, 22.58, 25.54, 22.91, 23.71, 26.02, 26.95, 28.35, 28.87, 29.12, 29.16, 29.25, 29.34, 29.42, 29.48, 29.53, 29.63, 30.32, 31.52, 31.74, 31.83, 38.48, 38.70, 68.11, 68.20, 101.53, 108.52, 124.06, 125.21, 128.33, 128.74, 130.80, 131.78, 133.71, 134.09, 135.48, 140.52, 160.22, 166.39, 167.06; HRMS. (MALDI, [M+H]$^+$), $C_{86}H_{129}N_2O_8$, Calc: 1317.9749, Found: 1317.9753.

15, tetraethyl 1,5-bis(3,5-bis(octyloxy)phenyl)anthracene-2,3,6,7-tetracarboxylate: Starting from **12**, the synthesis of tetraester **15** was carried out according to general procedure C while diethyl maleate (3 eq) was employed instead of fumaronitrile. The crude mixture was purified by flash chromatography (hexane/EA = 10/1) to give the pure product (overall yield from **11** over three steps = 32%). IR (KBr) ν/cm^{-1}: 1064, 1123, 1167, 1255, 1591, 1726, 2856, 2927; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.85 (t, J = 7.0 Hz, 12H), 1.06 (t, J = 7.0 Hz, 6H), 1.22–1.44 (m, 44H), 1.74–1.80 (m, 10H), 3.94 (t, J = 6.5 Hz, 8H), 4.13 (q, J = 7.0 Hz, 4H), 4.38 (q, J = 7.0 Hz, 4H), 6.54 (d, J = 2.0 Hz, 4H), 6.59 (t, J = 2.0 Hz, 2H), 8.35 (s, 2H), 8.62 (s, 2H);^{13}C NMR (125 MHz, $CDCl_3$): δ 13.73, 14.03, 14.12, 14.20, 22.60, 25.99, 29.19, 29.03, 31.75, 61.22, 61.66, 68.21, 104.53, 109.01, 125.76, 128.79, 130.46, 131.51, 132.03, 132.87, 137.98, 138.91, 159.99, 165.56, 168.37; HRMS. (FAB, M$^+$), $C_{70}H_{98}O_{12}$, Calc: 1130.7085, Found: 1130.7057.

15′, (4,8-bis(3,5-bis(octyloxy)phenyl)-anthracene-2,3,6,7-tetramethanol: Starting from tetraester **14**, the synthesis of crude tetraol **15′** was carried out according to general procedure D. IR (KBr) ν/cm^{-1}: 1056, 1165, 1435, 1464, 1593, 2856, 2927; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.83–0.87 (m, 12H), 1.23–1.43 (m, 40H), 1.74–1.80 (m, 8H), 2.77 (broad s, 2H), 3.24 (broad s, 2H), 3.93–3.96 (m, 8H), 4.69 (s, 4H), 4.91 (s, 4H), 6.47 (d, J = 2.0 Hz, 4H), 6.59 (t, J = 2.0 Hz, 2H), 7.85 (s, 2H), 7.99 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.06, 22.62, 26.04, 29.21, 29.27, 29.37, 31.78, 60.82, 65.20, 68.23, 100.64, 108.86, 126.38, 129.27, 131.06, 133.70, 136.88, 140.12, 140.33, 160.11, 160.25; HRMS. (FAB, M$^+$), $C_{62}H_{90}O_8$, Calc: 962.6636, Found: 962.6635.

16, 1,5-bis(3,5-bis(octyloxy)phenyl)anthracene-2,3,6,7-tetracarbaldehyde: Starting from tetraol **15′**, the synthesis of crude tetraldehyde **16** was carried out according to general procedure E. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (t, J = 6.8 Hz, 12H), 1.16–1.49 (m, 40H), 1.74–1.83 (m, 8H), 3.98 (t, J = 6.8 Hz, 8H), 6.55 (d, J = 2.0 Hz, 4H), 6.67 (t, J = 2.0 Hz, 2H), 8.45 (s, 2H), 8.51 (s, 2H), 10.12 (s, 2H), 10.62 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.08, 22.64, 26.05, 29.22, 29.36, 31.79, 68.42, 101.62, 109.61, 130.88, 130.97, 131.65, 132.67, 133.46, 133.57, 135.80, 148.72, 160.56, 192.10, 193.40.

17, 5,12-bis(3,5-bis(octyloxy)phenyl)pentacene-2,3,9,10-tetracarbonitrile: Starting from crude tetraldehyde **16**, the synthesis of pentacene tetranitrile **17** was accomplished according to general procedure C and purified by flash chromatography (CH_2Cl_2–hexane = 3/2) under nitrogen atmosphere to give the pure product (overall yield from **15** over three steps = 19%). IR (KBr) ν/cm^{-1}: 835, 1056, 1168, 1435, 1601, 2228, 2855, 2926; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83–0.85 (m, 12H), 1.25–1.52 (m, 40H), 1.80–1.82 (m, 8H), 4.00–4.03 (m, 8H), 6.57 (s, 4H), 6.77 (s, 2H), 8.25 (s, 2H), 8.41 (s, 2H), 8.75 (s, 2H), 8.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.02, 22.58, 26.03, 29.16, 29.23, 29.32, 31.74, 68.42, 101.48, 108.02, 109.71, 115.88, 116.11, 127.24, 128.68, 129.72, 130.74, 130.77, 131.25, 137.21, 137.72, 138.50, 141.53, 160.81; HRMS. (FAB, M$^+$), $C_{70}H_{82}O_4N_4$, Calc: 1042.6336, Found: 1042.6327.

18, tetraethyl 5,12-bis(3,5-bis(octyloxy)phenyl)pentacene-2,3,9,10-tetracarboxylate: Starting from crude tetraldehyde **16**, the synthesis of pentacene tetraester **18** was achieved according to general procedure C, but diethyl maleate (3 eq) was used instead of fumaronitrile. The crude mixture was purified by flash chromatography (CH_2Cl_2–hexane = 3/2) to give the product with minor impurities (overall yield from **15** over three steps = 17%). IR (KBr) ν/cm^{-1}: 1114, 1167, 1270, 1366, 1590, 1727, 2856, 2927; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82–0.85 (m, 12H), 1.23–1.45 (m, 50H), 1.75–1.82 (m, 10H), 3.93–4.01 (m, 8H), 4.32 (q, J = 6.8 Hz, 4H), 4.39 (q, J = 6.8 Hz, 4H), 6.62 (s, 4H), 6.72 (s, 2H), 8.07 (s, 2H), 8.36 (s, 2H), 8.68 (s, 2H), 8.75 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.01, 14.10, 14.14, 22.57, 26.01, 29.16, 29.25, 29.31, 29.63, 31.73, 60.60, 61.49, 68.26, 101.35, 109.80, 127.14, 127.85, 128.15, 128.28, 129.79, 129.95, 130.11, 130.66, 132.36, 138.99, 139.47, 160.43, 167.16, 167.97, 172.27; HRMS. (FAB, M$^+$), $C_{78}H_{102}O_{12}$, Calc: 1230.7371, Found: 1230.7388.

19, *N*,*N*′-bis-n-dodecyl- 5,12-bis(3,5-bis(octyloxy)phenyl)-pentacene-2,3,9,10-bisimide: Starting from crude tetraldehyde **16**, the synthesis of pentacene diimide **19** was achieved according to general procedure C, but *N*-n-dodecyl-maleimide (3 eq) was used instead of fumaronitrile. The crude mixture was purified by flash chromatography (CH_2Cl_2–hexane = 1/2) to give the pure product (overall yield from **15** over three steps = 57%). IR (KBr) ν/cm^{-1}: 1169, 1391, 1435, 1600, 1707, 1760, 2854, 2925; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82–0.86 (m, 18H), 1.22–1.31 (m, 68H), 1.42–1.48 (m, 12H), 1.66–1.68 (m, 6H), 1.77–1.85 (m, 10H), 3.73 (t, J = 7.2 Hz, 4H), 4.01 (t, J = 6.4 Hz, 8H), 6.61 (d, J = 2.0 Hz, 4H), 6.74 (t, J = 2.0 Hz, 2H), 8.23 (s, 2H), 8.39 (s, 2H), 8.77 (s, 2H), 8.79 (s, 2H);^{13}C NMR (100 MHz, $CDCl_3$): δ 14.01, 22.58, 25.54, 26.02, 26.86, 28.37, 29.16, 29.26, 29.32, 29.42, 29.54, 29.63, 31.73, 31.83, 38.40, 67.89, 68.27, 101.21, 109.73, 125.50, 126.24, 126.40, 128.50, 128.76, 129.69, 130.43, 130.76, 131.19, 131.99, 138.75, 142.23, 160.61, 167.43, 167.51; HRMS. (MALDI, [M+H]$^+$), $C_{94}H_{133}N_2O_8$, Calc: 1418.0062, Found: 1418.0068.

20, diethyl 6-(3,5-bis(octyloxy)benzoyl)-1-(3,5-bis(octyloxy)-phenyl)-7-formylnaphthalene-2,3-dicarboxylate: The unidirectional elongated product **20** was synthesized according to general procedure C from **12**. To ensure the right stochiometry the purity of starting dialdehyde **12** was calibrated with ^{1}H NMR using 1,4-dimethoxybenzene as an internal standard. 1.2 equivalents of diethyl maleate were used in the reaction. The crude mixture was purified by flash chromatography (CH_2Cl_2–hexane = 2/1) to give pure product (52%). IR (KBr) ν/cm^{-1}: 1063, 1169, 1263, 1443, 1593, 1728, 2856, 2927; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.84–0.87 (m, 12H), 1.07 (t, J = 7.0 Hz, 6H), 1.23–1.29 (m, 32H), 1.37–1.42 (m, 8H), 1.69–1.79 (m, 8H), 3.91–3.94 (m, 8H), 4.14 (q, J = 7.0 Hz, 2H), 4.41 (q, J = 7.0 Hz, 2H), 6.49 (d, J = 2.0 Hz, 2H), 6.56 (t, J = 2.0 Hz, 1H), 6.65 (t, J = 2.0 Hz, 1H), 6.86 (d, J = 2.0 Hz, 2H), 8.03 (s, 1H), 8.26 (s, 1H), 8.59 (s, 1H), 9.96 (s, 1H);^{13}C NMR (125 MHz, $CDCl_3$): δ 13.99, 22.57, 25.93, 25.96, 29.08, 29.12, 29.15, 29.24, 29.27, 31.73, 61.43, 61.98, 68.22, 68.38, 101.82, 106.56, 108.12, 108.96, 128.58, 130.09, 131.06, 133.00, 133.21, 133.59, 133.64, 135.06, 136.86, 137.71, 138.79, 140.37, 160.07, 160.34, 165.10, 167.72, 190.25, 195.73; HRMS. (FAB, M$^+$), $C_{62}H_{88}O_{10}$, Calc: 992.6377, Found: 992.6387.

20′, (4-(3,5-bis(octyloxy)phenyl)-7-((3,5-bis(octyloxy)phenyl)-(hydroxy)methyl)naphthalene-2,3,6-triyl)trimethanol: The reduction of **20** to tetraol **20′** was carried out according to general procedure D. IR (KBr) ν/cm^{-1}: 1056, 1166, 1385, 1459, 1595, 2856, 2926, 3339; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83–0.86 (m, 12H), 1.19–1.34 (m, 32H), 1.35–1.46 (m, 8H), 1.69–1.77 (m, 8H), 3.85–3.93 (m, 8H), 4.49 (d, J = 12.4 Hz, 1H), 4.58(d, J = 12.4 Hz, 1H), 4.66 (s, 2H), 4.92 (s, 2H), 6.07 (s, 1H), 6.36 (s, 1H), 6.39 (s, 1H), 6.50 (s, 2H), 6.52 (s, 1H), 7.39 (s, 1H), 7.75 (s, 1H), 7.81 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.04, 22.61, 26.02, 29.19, 29.25, 29.35, 31.77, 60.67, 64.51, 65.05, 68.09, 68.21, 75.09, 100.22, 100.52, 105.04, 108.79, 128.48, 128.65, 129.02, 131.87, 132.46, 134.66, 136.67, 138.01, 140.02, 140.22, 140.41, 144.99, 160.23, 160.43; HRMS. (MALDI, [M–OH+H]$^+$), $C_{58}H_{88}O_7$, Calc: 896.6530, Found: 896.6538.

21, 7-(3,5-bis(octyloxy)benzoyl)-4-(3,5-bis(octyloxy)phenyl)-naphthalene-2,3,6-tricarbaldehyde: Starting from **20′**, the synthesis of crude trialdehyde intermediate **21** was carried out according to general procedure E. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83–0.86 (m), 1.23–1.40 (m), 1.71–1.79 (m), 3.83–3.99 (m), 6.53–6.66(m), 6.86–6.87(m), 8.09 (s, 1H), 8.35 (s, 1H), 8.39 (s, 1H), 9.99 (s, 1H), 10.08 (s, 1H), 10.60 (s, 1H); ^{13}C spectrum can not be obtained due to rapid decomposition; HRMS. (FAB, [M+H]$^+$), $C_{58}H_{81}O_8$, Calc: 905.5931, Found: 905.5927.

22, 1,6-bis(3,5-bis(octyloxy)phenyl)tetracene-2,3,8,9-tetracarbonitrile: The synthesis of tetracene tetranitrile **22** was accomplished according to general procedure C and the crude product was purified by flash chromatography (CH_2Cl_2–hexane = 1/1) to give the pure tetracene product (overall yield from **20** over three steps = 52%). IR (KBr) ν/cm^{-1}: 1056, 1169, 1378, 1436, 1592, 2231, 2855, 2926; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83–0.86(m, 12H), 1.16–1.38 (m, 32H), 1.40–1.51 (m, 8H), 1.78–1.83 (m, 8H), 3.96–4.04 (m, 8H), 6.50 (d, J = 2.0 Hz, 2H), 6.60 (d, J = 2.0 Hz, 2H), 6.71 (t, J = 2.0 Hz, 1H), 6.74 (t, J = 2.0 Hz, 1H), 8.32 (s, 1H), 8.44 (s, 1H), 8.49 (s, 1H), 8.62 (s, 1H), 8.74 (s, 1H), 8.78 (s, 1H);^{13}C NMR (125 MHz, $CDCl_3$): δ 14.01, 22.58, 26.00, 29.16, 29.30, 29.63, 31.74, 68.47, 101.52, 102.63, 108.38, 108.82, 108.99, 109.01, 109.53, 109.62, 115.12, 115.62,

115.81, 115.85, 128.28, 129.49, 130.18, 130.60, 130.63, 131.39, 132.14, 136.05, 136.56, 137.60, 138.01, 142.01, 150.30, 160.79, 165.86; HRMS. (FAB, $[M+H]^+$), $C_{66}H_{81}O_4N_4$, Calc: 993.6258, Found: 993.6260.

23, *N*,*N*′-bis-n-dodecyl-1,6-bis(3,5-bis(octyloxy)phenyl)-tetracene-2,3,8,9-bisimide: The synthesis of tetracene diimide **23** was accomplished according to general procedure C and the crude product was purified by flash chromatography (EA/hexane = 1/19) to give the pure tetracene product (overall yield from **20** over three steps = 19%). IR (KBr) ν/cm^{-1}: 842, 1168, 1363, 1392, 1708, 1761, 2854, 2924; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82–1.77 (m, 98H), 1.77–1.83 (m, 8H), 3.65 (t, J = 7.2 Hz, 2H), 3.73 (t, J = 7.2 Hz, 2H), 3.96–3.99 (m, 8H), 6.55 (d, J = 2.0 Hz, 2H), 6.59 (d, J = 2.0 Hz, 2H), 6.69 (d, J = 2.0 Hz, 1H), 6.71 (d, J = 2.0 Hz, 1H), 8.30 (s, 1H), 8.39 (s, 1H), 8.45 (s, 1H), 8.60 (s, 1H), 8.70 (s, 1H), 8.80 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.05, 22.62, 26.07, 26.89, 27.02, 28.42, 29.20, 29.29, 29.37, 29.46, 29.58, 31.78, 31.87, 38.48, 68.25, 68.32, 101.32, 101.54, 108.55, 109.77, 122.88, 125.28, 125.90, 126.10, 126.85, 126.99, 127.23, 130.62, 130.72, 130.80, 131.44, 131.77, 131.99, 132.39, 132.99, 136.01, 138.32, 140.87, 142.39, 160.25, 160.67, 166.44, 167.16, 167.47, 167.55; HRMS. (MALDI, $[M+H]^+$), $C_{66}H_{80}N_2O_8$, Calc: 1367.9904, Found: 1367.9867.

24, tetraethyl 1,6-bis(3,5-bis(octyloxy)phenyl)tetracene-2,3,8,9-tetracarboxylate: The synthesis of tetracene tetraester **24** was accomplished according to general procedure C and the crude product was purified by flash chromatography (EA/hexane = 1/15) to give the pure tetracene product (overall yield from **20** over three steps = 23%). IR (KBr) ν/cm^{-1}: 1062, 1167, 1252, 1436, 1591, 1727, 2855, 2925; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86–1.43 (m, 64H), 1.75–1.80 (m, 8H), 3.91–4.01 (m, 8H), 4.13 (q, J = 7.2 Hz, 2H), 4.31–4.41 (m, 6H), 6.57–6.60 (m, 5H), 6.70 (s, 1H), 8.11 (s, 1H), 8.41 (s, 1H), 8.48 (s, 1H), 8.55 (s, 1H), 8.63 (s, 1H), 8.66 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.01, 14.13, 22.57, 26.01, 29.16, 29.30, 29.64, 31.74, 61.15, 61.56, 68.21, 68.31, 101.38, 101.60, 101.81, 109.01, 109.82, 122.56, 125.06, 127.64, 127.77, 128.54, 129.33, 129.45, 129.58, 129.81, 130.16, 130.33, 131.27, 131.66, 131.94, 133.60, 138.22, 138.78, 139.93, 160.00, 160.44, 165.68, 167.16, 167.91, 168.50; HRMS. (MALDI, $[M+H]^+$), $C_{74}H_{100}O_{12}$, Calc: 1181.7292, Found: 1181.7311.

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