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Synthesis and Fluorescence of a Series of Multichromophoric Acenaphthenyl Compounds

Ming Chen,[†] Kenneth P. Ghiggino,*[,†] San H. Thang,[‡] Jonathan White,[†] and Gerard J. Wilson[‡]

School of Chemistry, The University of Melbourne, Victoria 3010, Australia, and CSIRO Molecular Science, Bag 10, Clayton South, Victoria 3169, Australia

ghiggino@unimelb.edu.au

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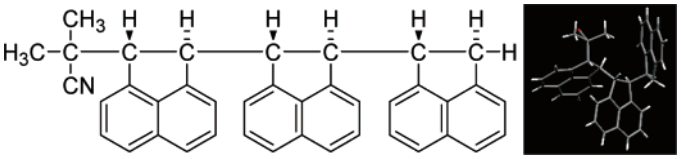

A novel free radical trapping reaction based on a stepwise radical reversible addition−fragmentation mechanism has been utilized to synthesize a series of acenaphthenyl dimers and trimers. The synthetic procedure involves the reaction of acenaphthylene with dithiobenzoate compounds (S=C(Ph)−SR) in the presence of a free radical initiator followed by reduction of the dithiobenzoyl end group with tributyltin hydride. Stereoisomers of the compounds have been isolated and their structures determined by proton NMR and X-ray crystallography. The solution fluorescence of the compounds has been characterized to reveal the requirements for intramolecular excimer (*exc*ited-state d*imer*) formation. Only in compounds containing identical stereochemical arrangements of adjacent acenaphthenyl groups is excimer fluorescence observed following photoexcitation.

Introduction

The fluorescence properties of linked multichromophoric molecules containing aromatic moieties of the same type often differ substantially from those of the constituent chromophores in dilute solution due to the additional process of excimer (*exci*ted-state d*imer*) formation.[1] Excimers form from the close association of a photoexcited and ground state chromophore pair and their stabilization as an excited state species arises from both charge transfer and exciton resonance interactions. The structure of an excimer is usually accepted to be a parallel sandwich configuration of the interacting chromophores with an interplanar distance of about 3 to 3.5 Å,[1,2] although studies of excimer formation in several multichromophoric systems have demonstrated that in some cases a parallel alignment is not strictly required and that sufficient stabilization can arise from a partially overlapped arrangement.[3] Molecules exhibiting excimer fluorescence have been used to probe the microviscosity of micelle and biological systems,[4] and excimers are believed to play a key role in determining the efficiency of light harvesting in aromatic polymers since they can act as traps for migrating excitons.[5]

Understanding the mechanisms of excimer formation in acenaphthenyl dimers and trimers is of key importance in resolving the origins of excimer fluorescence in poly(acenaphthylene) (PAcN).[6] Dilute solutions of PAcN display two distinct fluorescence bands: a short wavelength band (fluorescence maximum 335 nm), which is a mirror image of the absorption spectrum and can be assigned to emission from monomeric acenaphthenyl chromophores, and a broad structureless band at longer

* To whom correspondence should be addressed. Fax: +61-3-9347 5180. Phone: +61-3-8344 7137.

[†] The University of Melbourne.

[‡] CSIRO Molecular Science.

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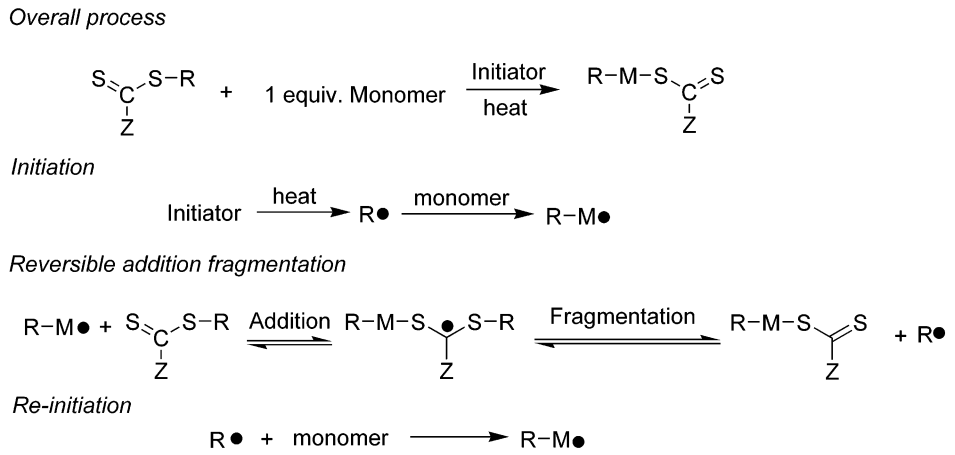
SCHEME 1



wavelengths (fluorescence maximum 420 nm) attributable to emission from intramolecular excimers. Examination of molecular models for sequences of PAcN has suggested that the reduced mobility of the pendant chromophores, which are attached rigidly to the polymer backbone by two carbon−carbon bonds, would not allow excimers to form between adjacent chromophores along the polymer backbone since they cannot adopt the required cofacial overlapped "sandwich" geometry of the aromatic groups required to maximize excimer stabilization. It has been proposed that next-to-nearest neighbor chromophore interactions could lead to excimer formation based on the observation of excimer emission in copolymers of acenaphthylene that have high degrees of alternation.[6a−g] On the other hand, more rigorous ground state molecular modeling and excited state semiempirical theoretical calculations have suggested that nearest-neighbor interactions cannot be entirely ignored.[6h,6i]

Over the past decades, great progress has been achieved in understanding the properties of free radicals.[7] An understanding of the kinetics and structure of free radicals has not only paved the way for development of new free radical reactions, but also led to the introduction of living radical polymerization.[8] Among them, the reactions based on reversible radical addition−fragmentation processes have attracted considerably interest both in organic synthesis and living radical polymerization.[9,10]

Recently, we reported a radical trapping reaction,[11] in which an unsaturated monomer was inserted into a thiocarbonylthio compound (S═C(Z)−SR) with the formation of a new carbon−carbon bond and a new carbon−sulfur bond (Scheme 1). It is based on the same reversible radical addition−fragmentation mechanism (RAFT) as previously described in controlled living radical polymerization.[10] The success of this radical addition reaction requires very fast rates of addition and fragmentation and efficient reinitiation. These characteristics are dependent on the nature of the R and Z groups. The general guidelines discussed previously for effective RAFT polymerization also apply here.[12] A similar radical mechanism has also been reported by Zard for the reaction of olefins with xanthates (Z = substituted oxygen).[10b,c] However, the *O*-alkyl xanthates used in that work have been shown to be a poor radical trap for styryl and (meth)acrylyl radicals, which has been attributed to the reduced C═S bond character caused by the interaction between the oxygen lone pairs and the C═S bond.[11b,13]

In the present study, this radical trapping reaction has been extended to synthesize a series of acenaphthenyl dimers and trimers (Scheme 2). After reduction of the

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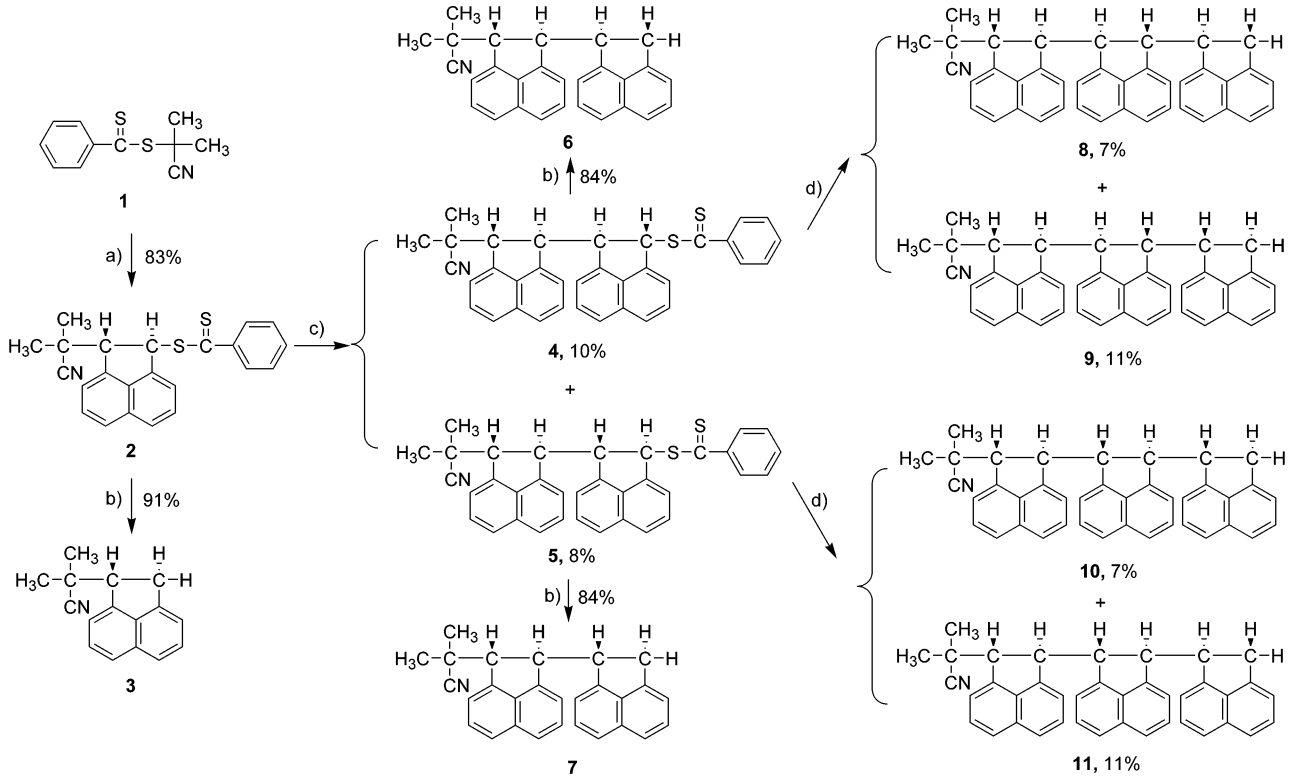
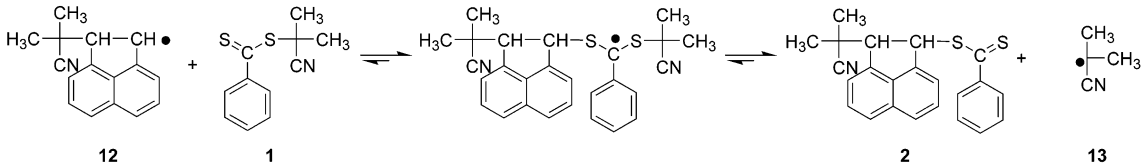
SCHEME 2[a]



[a] Reagents and conditions: (a) 1 equiv of acenaphthylene and 0.01 equiv of. AIBN in ethyl acetate, 70 °C, 20 h; (b) 4 equiv of Bu_3SnH and 0.01 equiv of AIBN in chlorobenzene, 80 °C, 4 h; (c) 2 equiv of acenaphthylene and 0.01 equiv of AIBN in toluene, 70 °C, 20 h; (d) 2 equiv of acenaphthylene and 0.01 equiv of AIBN in toluene, 70 °C, 24 h; then 4 equiv of Bu_3SnH and 0.01 equiv of AIBN in chlorobenzene, 80 °C, 4 h.

SCHEME 3



dithiobenzoyl end group using tributyltin hydride, the resulting acenaphthenyl compounds serve as model compounds to provide insight into the mechanisms of excimer formation in PAcN. Two diastereomers of the acenaphthenyl dimer, **6** and **7**, have been obtained. Four diastereomers of the trimer, **8**, **9**, **10**, and **11**, have been derived from the corresponding dimeric precursor. To allow for easy comparison of the relative configuration of the diastereomers, the enantiomer having the *R*-absolute configuration at the carbon adjacent to the 2-cyanopropan-2-yl end was used.

Results and Discussion

Synthesis of Acenaphthenyl Compounds with a Dithiobenzoyl End Group. Acenaphthylene was treated with 2-cyanopropan-2-yl dithiobenzoate[14] (**1**) in the presence of initiator 2,2′-azobis(isobutyronitrile) (AIBN) at 70 °C to give the required monomeric compound **2** after 20 h with 83% yield. The equilibrium involved in the reaction favors the right side, as the resulting 2-cyanopropan-2-yl radical (**13**) is more stable than the acenaphthenyl monomer radical (**12**) (Scheme 3). The structure of **2** has been identified by nuclear magnetic resonance (NMR) spectroscopy. The two protons of the five-membered ring are in the trans configuration. This result is in accord with the reversible addition−fragmentation process, which favors the more stable trans product.

The synthesis of acenaphthenyl dimers with the dithiobenzoyl group was undertaken using the reaction between compound **2** and acenaphthylene. The relatively low yield of the dimeric compounds, **4** and **5**, by this reaction can be explained by the following factors. As the leaving radicals here have similar properties, there is no preferred direction for the equilibrium (Scheme 4). The main function of the reversible radical addition−fragmentation process is to maintain the low active radical concentration in the solution to avoid the polymerization of the monomer and other radical−radical side reactions. During the process, the active monomeric radicals, **12**, can react with acenaphthylene to generate dimeric radicals, **14**. The dimeric radicals can be subsequently

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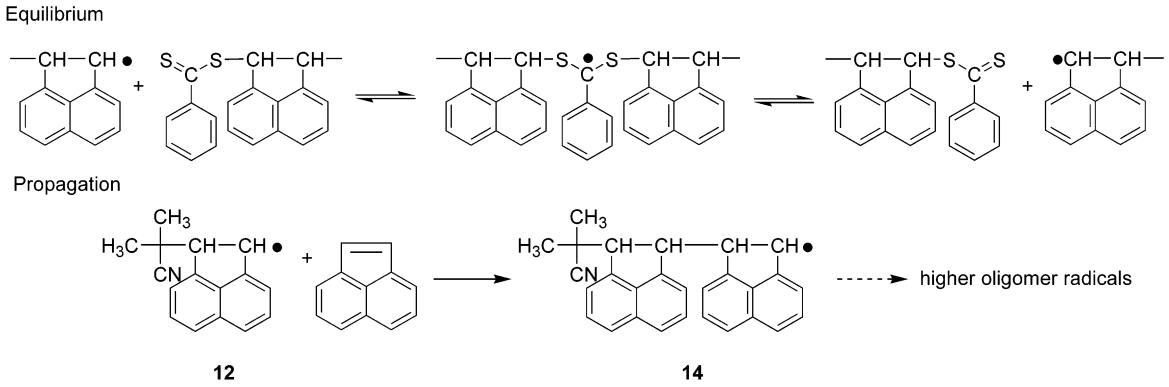
SCHEME 4



trapped by the thiocarbonylthio compound to produce the required acenaphthenyl dimers, or further propagate to generate radicals of trimer or higher oligomers. The latter process will lower the reaction yield.

Increasing the acenaphthylene feed ratio or using a higher temperature was found to increase the rate of reaction between monomeric radicals and acenaphthylene monomers, but it also increased the rate of side reactions involving dimeric radicals. In the present work, with 2 molar equiv of acenaphthylene and at 70 °C a reasonable yield was obtained. Higher oligomeric byproducts (ca. 5%) were observed after the reaction by HPLC analysis. Two diastereomers of the acenaphthenyl dimer, **4** and **5**, were isolated and the structures of these compounds were determined based on the results of 2D-NMR spectroscopy and X-ray crystal structural data for the corresponding desulfurized dimers. The structure of **5** was also determined by X-ray crystallography using crystals formed spontaneously during the preparative HPLC process (Figure 1).

Dimeric compound **4** contains a *threo*-disyndiotactic sequence, where the two acenaphthenyl units are enantiomeric. Compound **5** has a *threo*-diisotactic sequence, in which the two acenaphthenyl units have identical stereochemistry. The isolated yields of the two diastereoisomers are approximately the same with **4** slightly dominant (ca. 56%) (Note: the notation "*threo*-disyndiotactic" and "*threo*-diisotactic" has been used to describe the dimeric stereochemical sequence in PAcN).[6]

The two protons of the two five-membered rings in both dimers are in the trans configuration. The trans configuration of the acenaphthenyl unit closer to the dithiobenzoate group is related to the mechanism of the reversible addition−fragmentation process as mentioned above for monomeric compound **2**. The trans configuration of the second acenaphthenyl unit further away from the dithiobenzoate group can be attributed to the presence of the adjacent bulky 2-cyanopropan-2-yl group. The trans configuration is kinetically and thermodynamically favored when the active radicals attack the acenaphthylene monomer.

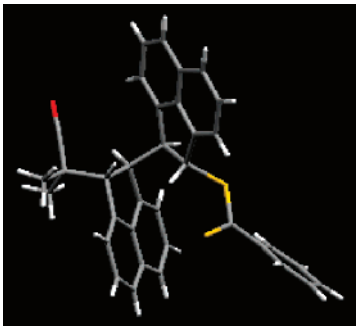


FIGURE 1. The crystal structure of **5**.

The synthesis of acenaphthenyl trimers with the dithiobenzoyl group proceeded similarly, and in total four diastereomers have been isolated.

Desulfurization by Tributyltin Hydride. As the dithiobenzoyl group can act as a quencher of excited acenaphthenyl chromophores as noted previously,[15] the dithiobenzoyl compounds were desulfurized by using an organotin reagent. Organotin hydrides have been extensively used as reducing agents in organic synthesis via a free radical mechanism.[16] The desulfurization process also involves a reversible radical addition−fragmentation process (Scheme 5).

Due to the affinity of tin for sulfur, the intermediate radical adduct fragments preferentially to give the acenaphthenyl radical R• and tributylstannyl dithiobenzoate. Hydrogen abstraction of the radical R• from tributyltin hydride leads to the desired acenaphthenyl compounds and a tributylstannyl radical to reinitiate the chain reaction. It was also observed that the desulfurization was incomplete when 1 molar equiv of tributyltin hydride was used. It is likely that the tributylstannyl dithiobenzoate can further trap another tributylstannyl radical to form an intermediate radical, which can irreversibly abstract hydrogen from another tributyltin hydride to provide a stable tin byproduct (see Scheme 5). However, attempts to isolate and identify these tin byproducts were unsuccessful. It is likely that these additional processes account for why 4 equiv of tributyltin hydride were required to yield the quantitatively desulfurized products.

Stereochemistry of the Desulfurized Acenaphthenyl Compounds. Reduction of the two diasteromers of the acenaphthenyl dimer with the dithiobenzoate group provided two corresponding dimers, in which **6** has a *threo*-disyndiotactic arrangement while **7** has a *threo*-

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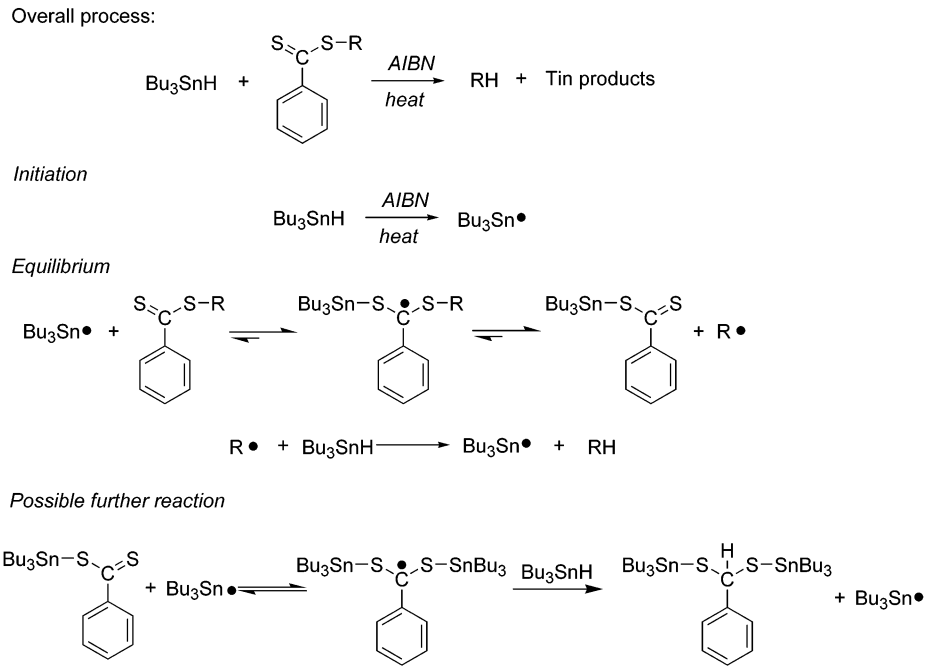
SCHEME 5



diisotactic arrangement. Four diasteromers of the acenaphthenyl trimer, **8**, **9**, **10** and **11**, were also similarly obtained. The structures of these six isomers have been determined by X-ray crystallography and 2D-NMR spectroscopy. Due to the factors mentioned previously, all the acenaphthenyl units of these compounds are in the trans configuration. The coupling constants between the protons of the five-membered rings of the acenaphthenyl units are consistent with previous reports.[17]

The crystal structures of all the dimers and trimers are presented in Figure 2, in which the assignments of the proton chemical shifts of these compounds in deuterated dichloromethane are also presented. The chemical shifts provide information on the molecular conformation in solution. A noticeable feature of the ^{1}H NMR spectra of these compounds is the relatively low chemical shifts (<6.5 ppm) of some of the aromatic protons (marked with an asterisk in Figure 2). All these protons belong to the acenaphthenyl unit with a *threo*-disyndiotactic configuration. The shift of these proton signals to high field can be attributed to the strong shielding effect of adjacent aromatic rings, indicating the protons are located in a region between the acenaphthenyl rings. It will be shown later that this "crossed" conformation of adjacent acenaphthenyl rings, with a *threo*-disyndiotactic arrangement, is unfavorable for excimer formation.

The structural studies also reveal that the adjacent acenaphthenyl rings in the ground state of all the compounds cannot readily adopt a parallel and fully overlapping geometry with each other at an interchromophore separation of the order of 3−3.5 Å, which is normally required for excimer formation, due to the conformational restrictions imposed by the five-membered ring of the acenaphthenyl unit. However, the *threo*-diisotactic sequence can more readily attain a partially overlapped configuration of the adjacent acenaphthenyl rings in contrast to a *threo*-disyndiotactic sequence. Previous theoretical calculations have predicted that it should be easier to achieve excimer stabilization in *threo*-diisotactic acenaphthenyl dimers.[6i]

The crystal structures also indicate that significant interactions between next-to-nearest neighboring acenaphthenyl rings to form excimers are also unlikely as the interplanar separations are considerably larger than 4 Å. However, dynamic interactions of the photoexcited molecules in solution do not totally exclude this possibility.

Fluorescence Studies of the Acenaphthenyl Compounds. The absorption spectra of the dimers and trimers resemble that of the acenaphthenyl monomer, **3**, with no evidence of electronic interaction between the acenaphthenyl units in the ground state.

The fluorescence spectra of the six dimers and trimers in dilute, degassed dichloromethane solutions (<10^{-5} M) are shown in Figure 3.

All compounds exhibit a structured emission with a wavelength maximum at approximately 340 nm, similar to the acenaphthenyl monomer **3**, which arises from the unassociated acenaphthenyl units. For compounds **6** and **9**, there is no evidence of any excimer emission at longer wavelengths. A very minor spectral component at longer wavelengths that might arise from excimer formation is just apparent in **8**. For **7**, **10**, and **11**, a strong excimer fluorescence band with maximum at approximately 410 nm is observed. All four compounds displaying excimer emission contain at least one *threo*-diisotactic sequence of the acenaphthenyl units. The compounds which contain one or two *threo*-disyndiotactic sequences of acenaphthenyl groups have no excimer emission. We conclude from these observations that excimer interactions can occur between adjacent acenaphthenyl units with a *threo*-

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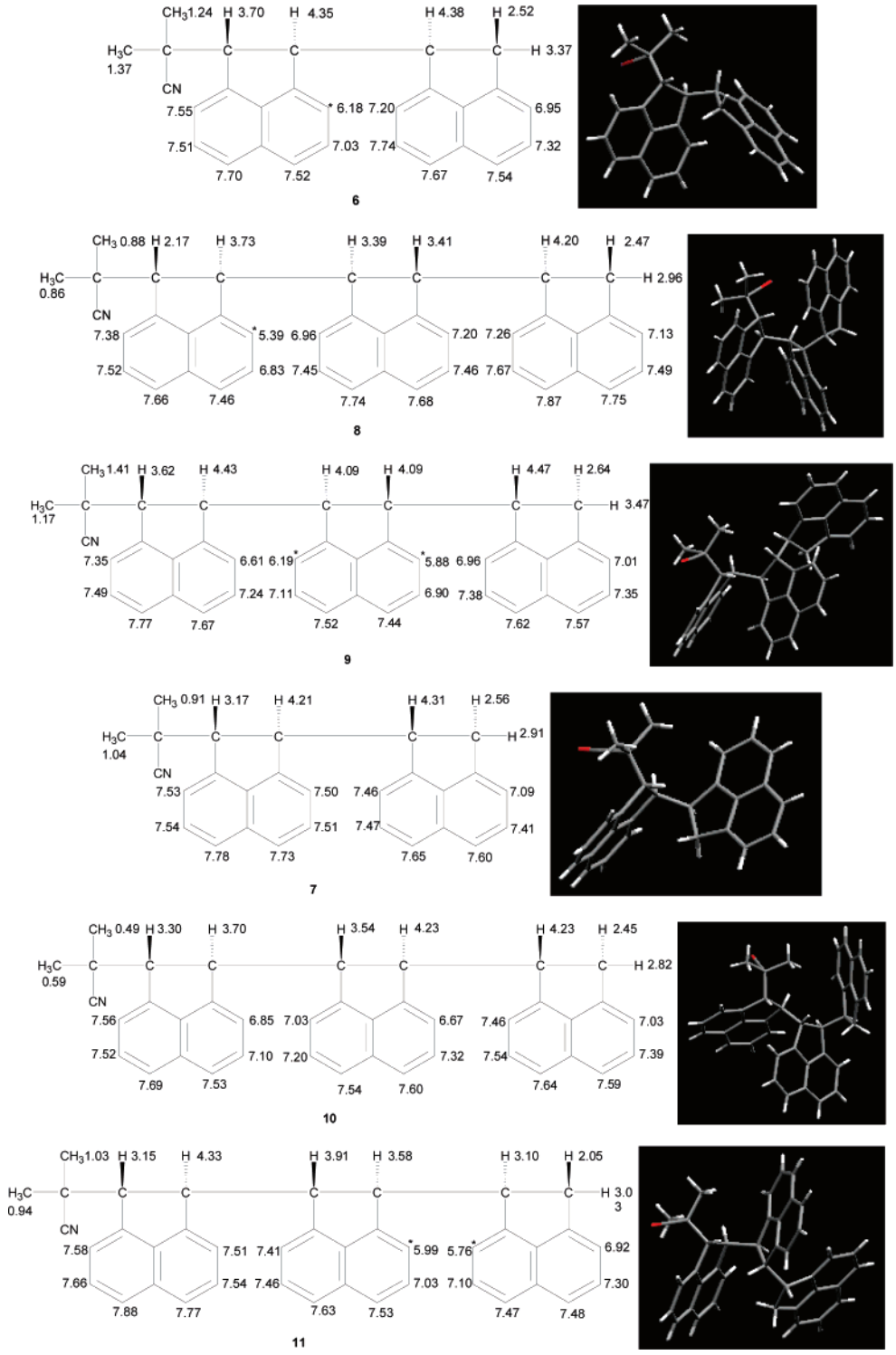

FIGURE 2. The ^1H chemical shifts in CD_2Cl_2 and crystal structures of the dimers and trimers obtained by 2D-NMR and X-ray crystallography, respectively.

diisotactic arrangement, while such interactions are absent between adjacent acenaphthenyl units with a *threo*-disyndiotactic sequence. This result is consistent with the conformational information obtained from NMR spectroscopy and X-ray crystallography and confirms a previous prediction from theoretical calculations.[6i] It should be noted that diluting the solutions 10-fold did not affect the excimer/monomer intensity ratio confirming that intramolecular interactions are responsible for the excimer emission observed.

While a fully overlapped planar "sandwich" configuration favors stable excimer formation, it appears not to be an absolute requirement for excimer formation in acenaphthenyl compounds in the *threo*-diisotactic arrangement, where only partial overlap of the acenaphthenyl rings appears possible. A similar dependence of

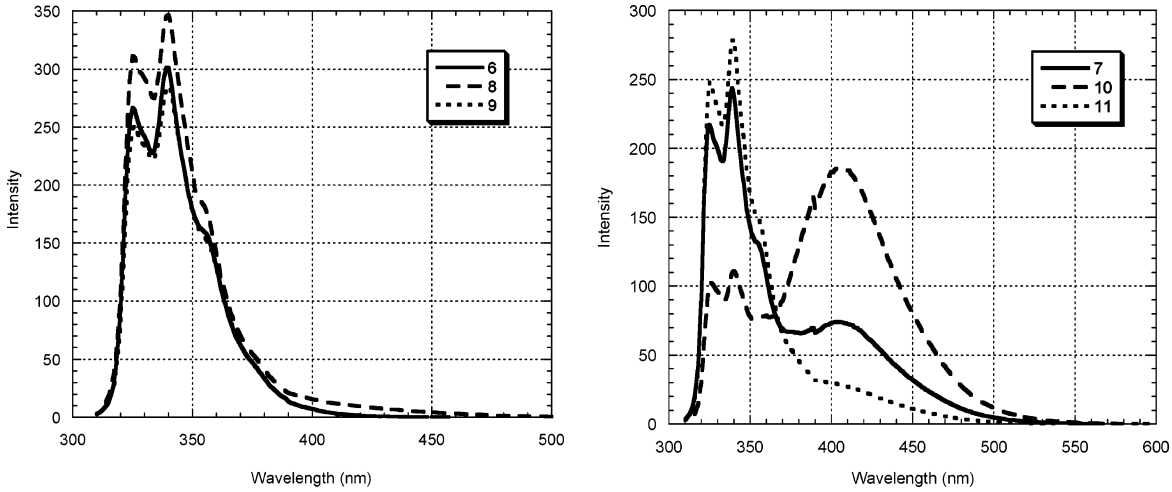

FIGURE 3. Fluorescence spectra of acenaphthenyl dimers and trimers in dilute, degassed dichloromethane solutions. All solutions have the same absorbance ($A = 0.10$) at the excitation wavelength of 295 nm.

excimer formation on stereochemical arrangement has also been proposed for excimer formation in poly(*N*-vinylcarbazole) and its model compounds.[3d,e]

The relative intensity of excimer emission can be characterized by the ratio of excimer to monomer intensity (I_{420nm}/I_{335nm}). This relative intensity varies in the four compounds containing the *threo*-diisotactic sequence: **7**, **8**, **10**, and **11**, indicating a complex role for the configuration of the acenaphthenyl unit adjacent to a *threo*-diisotactic sequence (see Figure 3).

The acenaphthenyl unit next to the excimer forming site can have three possible roles: (i) it can provide additional excimer formation sites; (ii) it can provide steric restrictions to affect the stability of the preformed excimer site; and (iii) it can be involved in energy transfer to the excimer formation site, and the efficiency of this energy transfer process will be dependent on the relative orientation of the chromophores.[18]

Based on the present results, it is not possible to discriminate between the relative importance of these factors. Kinetic studies of excimer formation and energy transfer in these dimers and trimers by time-resolved fluorescence methods should provide additional information.

Conclusions

A series of stereoisomeric acenaphthenyl dimers and trimers have been synthesized via a stepwise radical reversible addition−fragmentation process. An investigation of the photophysics of these dimers and trimers confirms that neighboring chromophores are indeed able to form excimers but the interaction is strongly dependent on the stereochemical arrangement of the acenaphthenyl moieties with the *threo*-diisotactic arrangement favored. Although a planar "sandwich" configuration may be desirable for stable excimer formation, it does not appear to be an absolute requirement for excimer formation in multichromophoric acenaphthenyl compounds.

Experimental Section

(1*RS*,2*RS*)-2-(2-Cyanopropan-2-yl)-acenaphthen-1-yl Dithiobenzoate (2). A mixture of 2-cyanopropan-2-yl dithiobenzoate (**1**) (1.00 g, 4.52 mmol), acenaphthylene (0.69 g, 4.52 mmol), AIBN (5 mg, 0.03 mmol), and ethyl acetate (2 mL) was degassed through 3 freeze−pump−thaw cycles, sealed under vacuum, and heated at 70 °C for 20 h. Purification by column chromatography on silica gel (Kieselgel-60, 70−230 mesh) with ethyl acetate:*n*-hexane = 5:95 (v/v) as eluent give the title compound as a red solid (1.40 g, 83%). Mp: 115−116 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$, ppm) δ 1.23 (s, 3H), 1.59 (s, 3H), 4.14 (br s, 1H), 6.32 (br s, 1H), 7.33−7.52 (m, 4H), 7.52−7.66 (m, 2H), 7.74 (d, 1H, J = 7.1 Hz), 7.79 (d, 1H, J = 7.4 Hz), 7.84 (d, 1H, J = 6.3 Hz), 8.05 (d, 2H, J = 7.4 Hz). ^{13}C (100.63 MHz, $CDCl_3$, ppm) δ 21.8, 25.4, 36.3, 53.7, 58.0, 120.3, 121.7, 124.5, 124.88, 124.92, 127.4, 128.3, 128.59, 128.64, 131.2, 133.1, 137.8, 140.3, 142.0, 144.3, 225.8. UV−vis (CH_2Cl_2), λ_{max} (log ϵ) 295 nm (4.36), 301 nm (shoulder, 4.36), 345 nm (shoulder, 3.83), 495 nm (2.13). HRMS (EI) calcd for $C_{23}H_{19}NS_2$ 373.0953, found 373.0947.

2-Acenaphthen-1-yl-2-methyl-propionitrile (3). A mixture of **2** (120 mg, 0.322 mmol), tributyltin hydride (Bu_3SnH) (376 mg, 1.288 mmol), AIBN (1 mg, 0.006 mmol), and chlorobenzene (0.5 mL) was degassed through 3 freeze−pump−thaw cycles, sealed under vacuum, and heated in a 80 °C oil bath for about 4 h until the solution became colorless. Purification by column chromatography on silica gel (Kieselgel-60, 70−230 mesh) with ethyl acetate:*n*-hexane = 5:95 (v/v) as eluent afforded the title compound as a white solid (65 mg, 91%). The product was recrystallized in methanol. Mp 89−90 °C. ^{1}H NMR (500.13 Hz, $CDCl_3$, ppm) δ 1.29 (s, 3H), 1.36 (s, 3H), 3.35 (dd, 1H, J = 17.67, 3.35 Hz), 3.58 (dd, 1H, J = 17.67, 8.39 Hz), 3.95 (dd, 1H, J = 8.39, 3.35 Hz), 7.28 (d, 1H, J = 6.9 Hz), 7.47 (m, 2H), 7.61 (d, 2H, J = 7.73 Hz), 7.68 (d, 1H, J = 8.19 Hz). ^{13}C (126.77 MHz, $CDCl_3$, ppm) δ 22.9, 24.5, 34.4, 36.4, 50.8, 119.5, 121.4, 123.0, 124.4, 125.6, 128.0, 128.2, 131.7, 139.5, 142.7, 143.1. UV−vis (CH_2Cl_2), λ_{max} (log ϵ) 289 nm (3.84), 300 nm (shoulder, 3.65). HRMS (EI) calcd for $C_{16}H_{15}N$ 221.1199, found 221.1199.

(1*SR*,2*SR*,1′*RS*,2′*RS*)-2′-(2-Cyanopropan-2-yl)-1,2,1′,2′-tetrahydro[1,1′]biacenaphthylene-2-yl Dithiobenzoate (4) and (1*RS*,2*RS*,1′*RS*,2′*RS*)-2′-(2-Cyanopropan-2-yl)-1,2,1′,2′-tetrahydro[1,1′]biacenaphthylene-2-yl Dithiobenzoate (5). A mixture of **2** (1.00 g, 2.68 mmol), acenaphthylene (0.82 g, 5.36 mmol), AIBN (5 mg, 0.03 mmol), and toluene (1.0 mL) was degassed through 3 freeze−pump−thaw cycles, sealed under vacuum, and heated at 70 °C for 20 h. Purification by column chromatography on silica gel (Kieselgel-60, 230−400 mesh) with ethyl acetate:*n*-hexane = 5:95 (v/v) as eluent afforded **4** and **5**.[19] **5** was further purified by preparative HPLC

(18) Förster, Th. *Ann. Phys.* **1948**, *2*, 55.

using a mixture of 2-propanol (0.5%), water (7.5%), and acetonitrile (92%) as the eluent.

4: 140 mg, 10%. ^{1}H NMR (500.13 Hz, CD_2Cl_2, ppm) δ 1.33 (s, 3H), 1.35 (s, 3H), 3.54 (br s, 1H), 4.51 (m, 1H), 4.66 (br s, 1H), 5.60 (d, 1H, J = 2.5), 6.55 (d, 1H, J = 6.9 Hz), 6.67 (d, 1H, J = 6.8 Hz), 7.15−7.24 (m, 2H), 7.25−7.34 (m, 2H), 7.38−7.47 (m, 4H), 7.56 (m, 1H), 7.64−7.77 (m, 4H), 7.97 (d, 2H, J = 7.9 Hz). ^{13}C (126.77 MHz, CD_2Cl_2, ppm) δ 24.0, 24.2, 37.4, 52.2, 55.0, 55.2, 57.9, 120.3, 120.7, 120.8, 122.2, 124.2, 124.3, 124.8, 125.0, 125.3, 127.4, 128.1, 128.2, 128.3, 128.6, 128.9, 131.4, 131.5, 133.1, 138.9, 140.1, 142.1, 142.4, 143.1, 143.5, 144.9, 227.3. UV−vis (CH_2Cl_2), λ_{max} (log ϵ) 294 nm (4.47), 340 nm (shoulder, 3.78). HRMS (EI) calcd for $C_{35}H_{27}NS_2$ 525.1585, found 525.1562.

5: 112 mg, 8%. Mp 204−205 °C. ^{1}H NMR (500.13 Hz, CD_2Cl_2, ppm) δ 1.08 (s, 3H), 1.21 (s, 3H), 3.48 (br s, 1H), 4.48 (m, 1H), 4.56 (d, 1H, J = 3.2 Hz), 5.56 (d, 1H, J = 4.0 Hz), 7.24 (d, 1H, J = 7.1 Hz), 7.31−7.39 (m, 3H), 7.40−7.46 (m, 3H), 7.47−7.53 (m, 3H), 7.54−7.60 (m, 2H), 7.62−7.71 (m, 5H). ^{13}C (126.77 MHz, CD_2Cl_2, ppm) δ 23.4, 25.1, 37.2, 50.5, 54.8, 58.1, 120.5, 120.6, 121.3, 122.4, 124.3, 124.75, 124.83, 125.1, 127.3, 128.11, 128.13, 128.4, 128.66, 128.68, 131.5, 131.9, 132.7, 138.6, 139.7, 142.0, 142.4, 143.0, 143.7, 145.0, 226.4. UV−vis (CH_2Cl_2), λ_{max} (log ϵ) 294 nm (4.46), 340 nm (shoulder, 3.78). HRMS (EI) calcd for $C_{35}H_{27}NS_2$ 525.1585, found 525.1572. Red needle crystals formed spontaneously during the preparative HPLC process were used as such for X-ray crystallography.

Crystal data for 5: $C_{35}H_{27}NS_2$, M = 525.70, T = 295 K, λ = 0.71069 Å, monoclinic, space group $P21/XXX$, a = 8.9492(12) Å, b = 22.822(3) Å, c = 13.7252(18) Å, β = 102.240(3)°, V = 2739.5(6) Å^3, Z = 4, D_x = 1.275 M gm^{-3}, μ(Mo Kα) = 0.219 mm^{-1}, F(000) = 1104, crystal size 0.5 × 0.05 × 0.01 mm^3. 14327 reflections measured, 4835 independent reflections (R_{int} = 0.1528) and the final $wR(F^2)$ was 0.0906 and final R was 0.0578 for 1711 unique data with [$I > 2\sigma(I)$].

2-Methyl-(1*RS*,2*RS*,1′*RS*,)-2-(1,2,1′,2′-tetrahydro[1,1′]-biacenaphthylene-2-yl)propionitrile (6). 6 was prepared as described above for **3** using **4** (50 mg, 0.095 mmol), Bu_3SnH (111 mg, 0.381 mmol), AIBN (1 mg, 0.006 mmol), and chlorobenzene (0.5 mL). Yield 30 mg, 84%. Mp 170−171 °C. ^{1}H NMR (500.13 Hz, CD_2Cl_2, ppm) δ 1.37 (s, 3H), 1.42 (s, 3H), 2.52 (br dd, 1H, J = 17.4, 3.7 Hz), 3.37 (br dd, 1H, J = 17.4, 8.1 Hz), 3.70 (m, 1H), 4.35 (m, 1H), 4.38 (m, 1H), 6.18 (d, 1H, J = 7.0 Hz), 6.95 (d, 1H, J = 6.8 Hz), 7.02 (dd, 1H, J = 8.2, 7.0 Hz), 7.20 (br d, J = 6.9 Hz), 7.32 (dd, 1H, J = 8.2, 6.9 Hz), 7.44−7.59 (m, 5H), 7.66 (d, 1H, J = 8.2 Hz), 7.70 (d, 1H, J = 8.0 Hz). ^{13}C (126.77 MHz, CD_2Cl_2, ppm) δ 23.87, 23.94, 33.0, 37.3, 49.3, 51.7, 56.7, 119.4, 119.8, 120.6, 121.8, 122.6, 123.6, 123.8, 124.8, 125.6, 128.0, 128.1, 128.16, 128.24, 131.4, 131.7, 140.1, 140.5, 142.1, 143.3, 144.8, 147.0. UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 290 nm (4.09), 301 nm (shoulder, 3.95). HRMS (EI) calcd for $C_{28}H_{23}N$ 373.1825, found 373.1824. Crystallization from a mixture of dichloromethane and methanol afforded crystals for X-ray crystallography.

Crystal data for 6: $C_{28}H_{23}N$, M = 373.47, T = 295 K, λ = 0.71069 Å, monoclinic, space group $P21/xxx$, a = 7.5426(10) Å, b = 12.0543(15) Å, c = 22.414(3) Å, β = 90.244(3)°, V = 2037.9(4) Å^3, Z = 4, D_x = 1.217 Mg m^{-3}, μ(Mo Kα) = 0.070 mm^{-1}, F(000) = 792, crystal size 0.4 × 0.05 × 0.03 mm^3. 10471 reflections measured, 3569 independent reflections (R_{int} = 0.1276) and the final $wR(F^2)$ was 0.0757 and final R was 0.0560 for 1151 unique data with [$I > 2\sigma(I)$].

2-Methyl-(1*RS*,2*RS*,1′*SR*)-2-(1,2,1′,2′-tetrahydro[1,1′]-biacenaphthylene-2-yl)propionitrile (7). 7 was prepared using **5** (50 mg, 0.095 mmol), Bu_3SnH (111 mg, 0.381 mmol), AIBN (1 mg, 0.006 mmol), and chlorobenzene (0.5 mL). Yield 30 mg, 84%. Mp 92−93 °C. ^{1}H NMR (500.13 Hz, CD_2Cl_2, ppm) δ 0.91 (s, 3H), 1.04 (s, 3H), 2.56 (br dd, 1H, J = 17.9, 3.4 Hz), 2.91 (br dd, 1H, J = 17.9, 8.4 Hz), 3.17 (s, 1H), 4.21 (m, 1H), 4.31 (m, 1H), 7.09 (br d, 1H, J = 6.9 Hz), 7.41 (dd, 1H, J = 8.2, 6.9 Hz), 7.45−7.57 (m, 6H), 7.60 (br d, 1H, J = 8.2 Hz), 7.65 (m, 1H), 7.73 (d, 1H, J = 8.2 Hz), 7.78 (br d, 1H, J = 7.9 Hz). ^{13}C (126.77 MHz, CD_2Cl_2, ppm) δ 23.2, 25.5, 33.3, 37.0, 50.4, 51.1, 53.5, 119.7, 119.8, 121.1, 122.0, 122.7, 123.7, 123.9, 124.8, 125.2, 128.0, 128.3, 128.4, 128.7, 131.5, 131.8, 139.7, 139.9, 143.2, 144.7, 146.08, 146.11. HRMS (EI) calcd for $C_{28}H_{23}N$ 373.1825, found 373.1824. UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 293 nm (4.16), 301 nm (shoulder, 4.04). Crystallization from a mixture of dichloromethane and ethanol afforded crystals for X-ray crystallography.

Crystal data for 7:[20] $(C_{28}H_{23}N)_2{\cdot}CH_2Cl_2$, M = 831.87, T = 295 K, λ = 1.5418 Å, triclinic, space group $P\bar{1}$, a = 10.5425(7) Å, b = 11.7920(5) Å, c = 19.307(2) Å, α = 88.382(6)°, β = 80.163(7)°, γ = 71.376(5)°, V = 2240.2(3) Å^3, Z = 4, D_x = 1.236 Mg m^{-3}, μ(Cu Kα) = 16.1 mm^{-1}, F(000) = 876, crystal size 0.5 × 0.25 × 0.04 mm^3. 8068 reflections measured, 7607 independent reflections (R_{int} = 0.0146) and the final $wR(F^2)$ was 0.2355 and final R was 0.0779, for 5480 unique data with [$I > 2\sigma(I)$].

(1*RS*,2*RS*,1′*RS*,2′*RS*,1″*RS*)-2-(1,2,1′,2′,1″,2″-Hexahydro-[1,1′:2′,1″]teracenaphthylene-2-yl)-2-methylpropionitrile (8) and (1*RS*,2*RS*,1′*RS*,2′*RS*,1″*SR*)-2-(1,2,1′,2′,1″,2″-hexahydro[1,1′:2′,1″]teracenaphthylene-2-yl)-2-methylpropionitrile (9). A mixture of **4** (200 mg, 0.381 mmol), acenaphthylene (116 mg, 0.762 mmol), AIBN (4 mg, 0.024 mmol), and toluene (1.0 mL) was degassed through 3 freeze−pump−thaw cycles, sealed under vacuum, and heated at 70 °C for 24 h. After the unreacted acenaphthylene monomer was removed by column chromatography on silica gel (Kieselgel-60, 70−230 mesh) with ethyl acetate:*n*-hexane = 1:9 (v/v) as eluent, the mixture was then desulfurized using Bu_3SnH (444 mg, 1.524 mmol). After removal of tin agents and other byproducts by column chromatography on silica gel (Kieselgel-60, 70−230 mesh) with ethyl acetate:*n*-hexane = 5:95 (v/v) as eluent, the mixture was purified by preparative reverse phase HPLC, using a mixture of 2-propanol (0.5%), water (7.5%), and acetonitrile (92%) as the eluent, to afford **8** (14 mg, 7%) and **9** (23 mg, 11%). Both stereoisomers were crystallized from a mixture of dichloromethane and methanol to afford crystals for X-ray crystallography.

8: Mp 218−219 °C. ^{1}H NMR (500.13 Hz, CD_2Cl_2, ppm) δ 0.86 (s, 3H), 0.88 (s, 3H), 2.17 (br s, 1H), 2.47 (br d, 1H, J = 17.7 Hz), 2.96 (br dd, 1H, J = 17.7, 8.1 Hz), 3.39 (m, 1H), 3.41 (s, 1H), 3.73 (m, 1H), 4.20 (br d, 1H, J = 8.1 Hz), 5.39 (d, 1H, J = 7.0 Hz), 6.83 (dd, 1H, J = 8.1, 7.1 Hz), 6.96 (d, 1H, J = 6.2 Hz), 7.13 (d, 1H, J = 6.8 Hz), 7.20 (d, 1H, J = 6.9 Hz), 7.26 (d, 1H, J = 6.8 Hz), 7.38 (d, 1H, J = 7.0 Hz), 7.42−7.55 (m, 5H), 7.63−7.71 (m, 3H), 7.74 (m, 2H), 7.87 (d, 1H, J = 8.2 Hz). ^{13}C (126.77 MHz, CD_2Cl_2, ppm) δ 23.8, 23.9, 33.0, 36.8, 49.2, 50.8, 51.7, 52.8, 55.3, 119.3, 119.9, 120.0, 120.4, 122.1, 122.8, 123.4, 123.6, 123.8, 124.2, 124.5, 124.9, 127.8, 127.9, 128.4, 128.56, 128.61, 128.7, 131.3, 131.4, 132.0, 139.9, 140.1, 140.2, 142.5, 143.5, 145.3, 146.9, 147.8, 148.0. HRMS (EI) calcd for $C_{40}H_{31}N$ 525.2451, found 525.2444. UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 295 nm (4.29), 303 nm (shoulder, 4.16).

Crystal data for 8: $C_{40}H_{31}N$, M = 525.66, T = 295 K, λ = 0.71069 Å, triclinic, space group $P\bar{1}$, a = 10.014(3) Å, b = 11.776(3) Å, c = 12.422(3) Å, α = 93.439(6)°, β = 103.626(5)°, γ = 91.543(6)°, V = 1419.8(6) Å^3, Z = 2, D_x = 1.230 Mg m^{-3}, μ(Mo Kα) = 0.070 mm^{-1}, F(000) = 556, crystal size 0.4 × 0.04 × 0.04 mm^3. 7478 reflections measured, 4892 independent reflections (R_{int} = 0.1167) and the final $wR(F^2)$ was 0.1252 and final R was 0.0712 for 1493 unique data with [$I > 2\sigma(I)$].

9: Mp 215−216 °C. ^{1}H NMR (500.13 Hz, CD_2Cl_2, ppm) δ 1.17 (s, 3H), 1.41 (s, 3H), 2.64 (br dd, 1H, J = 17.4, 3.6 Hz), 3.47 (br dd, 1H, J = 17.4, 8.3 Hz), 3.62 (br s, 1H), 4.09 (m, 2H), 5.88 (d, 1H, J = 7.0 Hz), 6.19 (d, 1H, J = 6.6 Hz), 6.61 (d, 1H, J = 6.9 Hz), 6.90 (dd, 1H, J = 8.0, 7.1 Hz), 6.96 (d, 1H, J

(19) There were three red bands during the column chromatography. The first belongs to the unreacted **2**. The second is compound **4**, and the third is compound **5** mixed with some higher oligomers.

(20) The crystals of **7** contained two molecules of the dimer and one CH_2Cl_2 in one asymmetric unit.

= 6.9 Hz), 7.01 (d, 1H, J = 6.9 Hz), 7.11 (m, 1H), 7.24 (dd, 1H, J = 8.0, 7.0 Hz), 7.32−7.40 (m, 3H), 7.44 (d, 1H, J = 8.2 Hz), 7.47−7.53 (m, 2H), 7.57 (d, 1H, J = 8.1 Hz), 7.62 (d, 1H, J = 8.3 Hz), 7.67 (d, 1H, J = 8.2 Hz), 7.77 (d, 1H, J = 8.3 Hz). ^{13}C (126.77 MHz, CD_2Cl_2, ppm) δ 23.2, 24.3, 33.7, 37.6, 48.6, 51.0, 52.7, 55.0, 55.5, 119.4, 119.8, 120.08, 120.13, 120.2, 122.0, 122.6, 123.3, 123.4, 123.6, 123.9, 124.0, 124.9, 125.9, 127.7, 127.8, 128.1, 128.24, 128.25, 128.4, 131.2, 131.4, 131.6, 140.1, 140.6, 140.7, 142.0, 144.59, 144.64, 145.0, 147.6. HRMS (EI) calcd for $C_{40}H_{31}N$ 525.2451, found 525.2448. UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 294 nm (4.31), 302 nm (shoulder, 4.16).

Crystal data for 9: $C_{40}H_{31}N$, M = 525.66, T = 295 K, λ = 0.71069 Å, triclinic, space group $P\bar{1}$, a = 7.484(2) Å, b = 12.286(4) Å, c = 16.015(5) Å, α = 101.624(7)°, β = 91.596(6)°, γ = 101.812(7)°, V = 1408.1(7) Å^3, Z = 2, D_x = 1.240 Mg m^{-3}, μ(Mo Kα) = 0.071 mm^{-1}, F(000) = 556, crystal size 0.3 × 0.1 × 0.01 mm^3. 7477 reflections measured, 4919 independent reflections (R_{int} = 0.0618) and the final $wR(F^2)$ was 0.0803 and final R was 0.0531 for 2000 unique data with [$I > 2\sigma(I)$].

(1*RS*,2*RS*,1′*SR*,2′*SR*,1″*SR*)-2-(1,2,1′,2′,1″,2″-Hexahydro-[1,1′:2′,1″]teracenaphthylene-2-yl)-2-methylpropionitrile (10) and (1*RS*,2*RS*,1′*SR*,2′*SR*,1″*RS*)-2-(1,2,1′,2′,1″,2″-Hexahydro[1,1′:2′,1″]teracenaphthylene-2-yl)-2-methylpropionitrile (11). 10 and **11** were similarly prepared from **5**. The eluent for preparative reverse phase HPLC was a mixture of 2-propanol (0.5%), water (15.0%), and acetonitrile (84.5%). Yield: **10** (14 mg, 7%) and **11** (23 mg, 11%). Both stereoisomers were crystallized from a mixture of dichloromethane/methanol to afford crystals for X-ray crystallography.

10: Mp 214−215 °C. ^{1}H NMR (500.13 Hz, CD_2Cl_2, ppm) δ 0.49 (s, 3H), 0.59 (s, 3H), 2.45 (br dd, 1H, J = 17.7, 3.4 Hz), 2.82 (br dd, 1H, J = 17.7, 7.9 Hz), 3.30 (br s, 1H), 3.54 (m, 1H), 3.70 (m, 1H), 4.23 (m, 2H), 6.67 (br s, 1H), 6.85 (d, 1H, J = 7.0 Hz), 7.03 (m, 2H), 7.10 (dd, 1H, J = 8.2, 7.0 Hz), 7.20 (m, 1H), 7.32 (m, 1H), 7.39 (dd, 1H, J = 8.2, 6.9 Hz), 7.46 (d, 1H, J = 6.9 Hz), 7.49−7.62 (m, 7H), 7.64 (d, 1H, J = 8.2 Hz), 7.69 (d, 1H, J = 8.0 Hz). ^{13}C (126.77 MHz, CD_2Cl_2, ppm) δ 21.7, 25.1, 33.0, 36.8, 49.4, 52.0, 52.3, 52.5, 55.7, 119.4, 119.5, 119.6, 120.0, 120.3, 121.5, 122.6, 123.2, 123.5, 123.6, 123.7, 124.6, 125.0, 128.0, 128.1, 128.3, 128.56, 128.61, 128.8, 131.3, 131.4, 132.0, 139.7, 139.8, 139.9, 142.9, 144.1, 144.9, 145.4, 146.8, 147.2. HRMS (EI) calcd for $C_{40}H_{31}N$ 525.2451, found MS 525.2445. UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 294 nm (4.35), 302 nm (shoulder, 4.23).

Crystal data for 10: $C_{40}H_{31}N$, M = 525.66, T = 295 K, λ = 0.71069 Å, monoclinic, space group *P21/XXX*, a = 8.099(2) Å, b = 13.782(4) Å, c = 25.681(7) Å, β = 95.354(6)°, V = 2854.0(13) Å^3, Z = 4, D_x = 1.223 Mg m^{-3}, μ(Mo Kα) = 0.070 mm^{-1}, F(000) = 1112, crystal size 0.4 × 0.4 × 0.04 mm^3. 14687 reflections measured, 5024 independent reflections (R_{int} = 0.1686) and the final $wR(F^2)$ was 0.0837 and final R was 0.0570 for 1370 unique data with [$I > 2\sigma(I)$].

11: Mp 168−169 °C. ^{1}H NMR (500.13 Hz, CD_2Cl_2, ppm) δ 0.94 (s, 3H), 1.03 (s, 3H), 2.05 (br dd, 1H, J = 17.2, 2.9 Hz), 3.03 (br dd, 1H, J = 17.2, 8.4 Hz), 3.10 (m, 1H), 3.15 (br s, 1H), 3.59 (m, 1H), 3.91 (m, 1H), 4.33 (br d, 1H, J = 2.5 Hz), 5.76 (d, 1H, J = 6.9 Hz), 5.99 (d, 1H, J = 6.9 Hz), 6.92 (d, 1H, J = 6.9 Hz), 7.03 (dd, 1H, J = 8.0, 7.1 Hz), 7.10 (dd, 1H, J = 8.1, 7.1 Hz), 7.30 (dd, 1H, J = 8.2, 6.9 Hz), 7.41 (d, 1H, J = 7.1 Hz), 7.44−7.59 (m, 7H), 7.61−7.68 (m, 2H), 7.77 (d, 1H, J = 8.0 Hz), 7.88 (d, 1H, J = 8.3 Hz). ^{13}C (126.77 MHz, CD_2Cl_2, ppm) δ 23.4, 25.4, 33.4, 37.0, 48.0, 50.2, 51.3, 53.9, 55.6, 119.0, 119.3, 120.09, 120.10, 120. 8, 122.3, 122.4, 123.0, 123.4, 123.9, 124.2, 125.0, 125.1, 127.95, 127.97, 128.10, 128.14, 128.5, 128.7, 131.4, 131.5, 131.7, 139.8, 139.9, 140.3, 143.3, 145.01, 145.02, 145.1, 145.7, 147.4. HRMS (EI) calcd for $C_{40}H_{31}N$ 525.2451, found 525.2441. UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 294 nm (4.34), 302 nm (shoulder, 4.21).

Crystal data for 11: $C_{40}H_{31}N$, M = 525.66, T = 295 K, λ = 0.71069 Å, triclinic, space group $P\bar{1}$, a = 11.1642(15) Å, b = 11.6529(16) Å, c = 12.7118(17) Å, α = 82.228(3)°, β = 67.199(3)°, γ = 70.834(3)°, V = 1440.0(3) Å^3, Z = 2, D_x = 1.212 Mg m^{-3}, μ(Mo Kα) = 0.069 mm^{-1}, F(000) = 556, crystal size 0.2 × 0.2 × 0.01 mm^3. 7611 reflections measured, 5012 independent reflections (R_{int} = 0.0417) and the final $wR(F^2)$ was 0.0705 and final R was 0.0477 for 2407 unique data with [$I > 2\sigma(I)$].

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Supporting Information Available: General experimental methods and the ^{1}H and ^{13}C NMR spectra of **2**−**11**, as well as crystallographic information files (CIFs) of **5**−**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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