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Synthesis of Highly Fluorescent Y-Enyne Dendrimers with Four and Six Arms[†,‡]

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Abstract: A first generation of dendrimeric Y-enynes with extended flexible chains was synthesized using Sonogashira coupling. Dendrimers **9** and **10** are highly fluorescent in the solid state and in solution.

Interest in cross-conjugated enynes (Y-enynes) has grown recently as a result of their unique conjugation, electronic, and photonic properties.[1−3] Fomina[4] first reported that polymerization of *β*,*β*-dibromo-4-ethynylstyrene produced a conjugated Y-enyne hyperbranched polymer.[5] Dendrimers have been thought to have a wide range of applications in biomedicine,[6] electronics,[7,8] sensors,[9−11] and coatings.[12,13] Twenty-five years ago, Chandrasekhar[14] discovered discotic liquid crystals[15] that constitute a unique class of materials.[16] Self-organization into structures with columnar order and liquidlike dynamics occurs in disk-shaped molecules with rigid aromatic cores and flexible peripheral side chains.[17] Molecules with flat disklike cores and surrounding alkyl substituents form columnar mesophases.[18]

In this paper, we report the synthesis of the first generation of Y-enyne dendrimers with four and six extended dodecyloxy arms, **9** and **10**, respectively (Scheme 1). The synthetic approach of **9** and **10** is a combination of both divergent[19] (four and six couplings) and convergent methods (acetylene **4** was synthesized separately). 4-Hydroxybenzaldehyde **1** was refluxed with 1-bromododecane[20] to afford 4-dodecyloxybenzaldehyde **2**, which was converted via Corey−Fuchs[21] reaction to 4-dodecyloxy-*β*,*β*-dibromostyrene **3**. The latter when reacted with *n*-BuLi afforded 1-dodecyloxy-4-ethynylbenzene **4**.[22] Terephthalaldehyde **5** and 1,3,5-benzenetricarboxaldehyde **7** were converted into 1,4-bis(2,2-dibromovinyl)benzene **6** and 1,3,5-tris(2,2-dibromovinyl)benzene **8**. Sonogashira[23] couplings of **6** and **4** as well as **8** and **4** afforded dendrimers **9** and **10**, respectively.[24] Differential scanning calorimetry (DSC) and optical polarized microscope measurements of **9** and **10** showed the absence of mesophase in these two compounds. The electron acceptor 2,4,7-trinitro-9-fluorenone (TNF) is commonly used in charge-transfer complexes to induce mesophase.[25] Preliminary results showed that charge-transfer complexes of **9**/TNF and **10**/TNF induced discotic mesophases in both systems.[26,27] A possible explanation for the absence of mesophase in **9** and **10** is the close proximity

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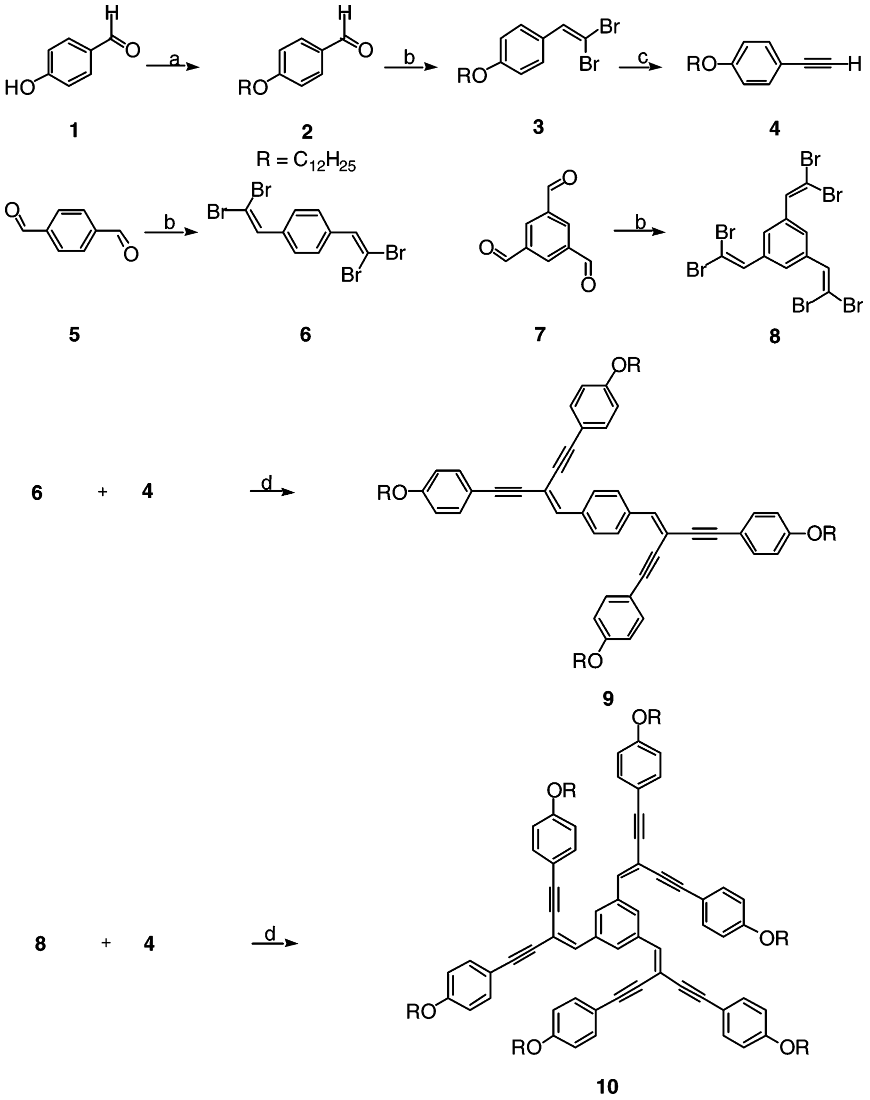
SCHEME 1. Synthesis of 9 and 10[a]



[a] (a) K_2CO_3, 2-butanone, $C_{12}H_{25}Br$, reflux (110 °C), argon, 24 h. (b) CH_2Cl_2, PPh_3, CBr_4, ice−H_2O bath, argon, 6 h. (c) *n*-BuLi, anhydrous THF, −78 °C (2 h) to rt (3 h); argon. (d) $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF, NEt_3, 70 °C.

of the tip to the core; this might be overcome with additional spacers to the cores of **9** and **10**, e.g., phenylethynyl groups.

Both **9** and **10** are highly fluorescent in solution and in the solid state. The absorption and emission of **9** are red shifted with respect to those of **10**; therefore, the π-system of **9** is more conjugated than that of **10**. This is due to the *meta* linkage in **10**. The better π-system conjugation of **9** has resulted in higher fluorescence quantum yield than in **10**. The photophysical properties of **9** and **10** are shown in Table 1. The emission spectra of **9** and **10** in ethyl acetate are shown in Figure 1.

TABLE 1. Photophysical Properties of 9 and 10 in Ethyl Acetate

compound	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	ϕ_f
9	428	485	0.51[a]
10	347	428	0.35[b]

[a] Coumarin 6 was used as actinometer (ϕ_f = 0.6 in cyclohexane[28]). [b] 9,10-Dimethyl anthracene was used as actinometer (ϕ_f = 0.9 in cyclohexane[29]).

Experimental Section

All manipulations were performed under argon. Reagents were purchased and used without further purification. CH_2Cl_2 was dried over CaH_2; THF was dried over sodium. Chemical shifts are in ppm with TMS as the internal standard (^1H NMR). Fluorescence spectra were recorded using both excitation and emission double-beam monochromators. All spectra were uncorrected and were measured in perpendicular geometry using 1-cm quartz cuvettes. Fluorescence quantum yields are relative to coumarin 6 for **9** and 9,10-dimethylanthracene for **10** as the external standards. All solutions were degassed with argon for 5 min.

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(26) Intramolecular and intermolecular interactions, such as ionic, H-bond, and charge transfer (CT) interactions, play an important role in the phase formation of liquid crystals. Discotic mesogens have proven to be very suitable for CT complexation: Praefcke, K.; Singer, D. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J. W., Gray, G. W., Spiess, H. W., Vill, V., Eds.; Wiley-VCH: New York, 1998; Vol. 2B, pp 945−967. Discotic mesogens can act as electron-rich donors when they are complexed with flat electron-poor molecules, because of their extended aromatic core: Kouwer, P. H. J.; Jager, W. F.; Mijs, W. J.; Picken, S. J. *Macromolecules* **2002**, *35*, 4322−4329.

(27) Further investigation of these systems is currently ongoing.

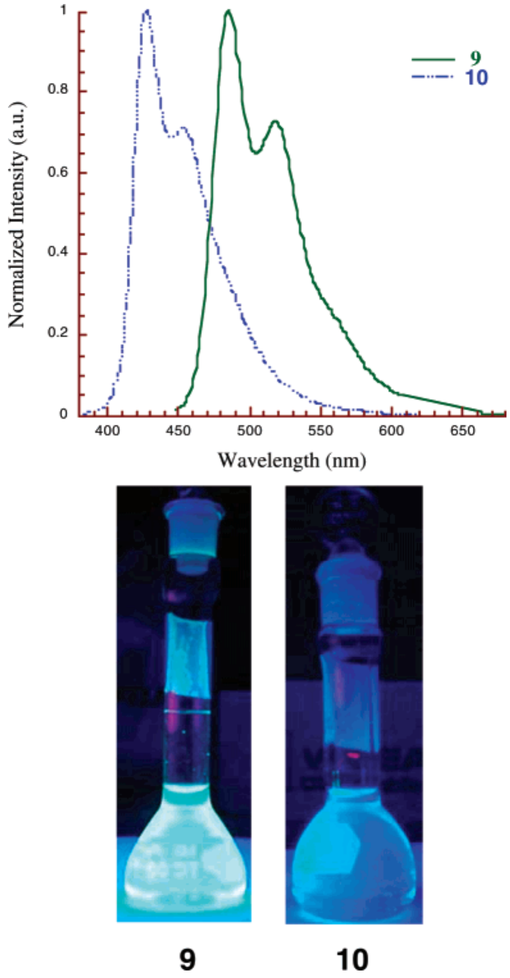

FIGURE 1. Emission of **9** and **10** in ethyl acetate (λ_{ex} (**9**) = 428 nm; λ_{ex} (**10**) = 347 nm).

The fluorescence quantum yield, ϕ_f, was calculated according to eq 1.[30] ϕ_{std} is the fluorescence quantum yield of the standard;

$$\phi_f = \phi_{std}\left(\frac{I_{unk}}{A_{unk}}\right)\left(\frac{A_{std}}{I_{std}}\right)\left(\frac{\eta_{unk}}{\eta_{std}}\right)^2 \qquad (1)$$

$I_{unk}$and I_{std} are the integrated emission intensities of the sample and the standard, respectively; A_{unk} and A_{std} are the absorbance of the sample and standard, respectively, at the desired wavelength λ_{ex}; and η_{unk} and η_{std} are the indexes of refraction of the sample and standard solutions, respectively.

4-Dodecyloxybenzaldehyde (2). This compound was synthesized according to a modified literature report.[20] ^{1}H NMR (200 MHz, $CDCl_3$): 0.85−0.91 (t, 3 H, CH_3), 1.21−1.32 (m, 16 H), 1.78−1.85 (t, 2 H, $OCH_2CH_2CH_2$), 3.37−3.42 (t, 2 H, OCH_2CH_2), 4.00−4.07 (t, 2 H, OCH_2), 6.97−7.01 (d, 2 H, *J* = 8.8 Hz, *m*-H to COH), 7.81−7.85 (d, 2 H, *J* = 8.8 Hz, *o*-H to COH), 9.88 (s, 1 H, COH).

4-Dodecyloxy-*β*,*β*-dibromostyrene (3). This compound was synthesized according to a modified literature report.[31] ^{1}H NMR (200 MHz, $CDCl_3$): 0.85−0.88 (t, 3 H, CH_3), 1.08−1.42 (m, 16 H), 1.72−1.89 (sextet, 2 H, $OCH_2CH_2CH_2$), 3.38−3.44 (t, 2 H, OCH_2CH_2), 3.93−3.99 (t, 2 H, OCH_2), 6.85−6.90 (d, 2 H, *J* = 8.8 Hz, *m*-H to $CHBr_2$), 7.40 (s, 1 H, $CHBr_2$), 7.48−7.52 (d, 2 H, *J* = 8.8 Hz, *o*-H to $CHBr_2$).

1-Dodecyloxy-4-ethynylbenzene (4). This compound was synthesized according to a modified literature procedure.[22] ^{1}H NMR (200 MHz, $CDCl_3$): 0.85−0.91 (t, 3 H, CH_3), 1.23−1.43 (m, 18 H), 1.70−1.84 (sextet, 2 H, OCH_2CH_2), 2.99 (s, 1 H, CCH), 3.91−3.98 (t, 2 H, OCH_2), 3.93−3.99 (t, 2 H, OCH_2), 6.80−6.85 (d, 2 H, *J* = 8.8 Hz, *m*-H to CCH), 7.39−7.44 (d, 2 H, *J* = 8.8 Hz, *o*-H to CCH).

1,4-Bis(2,2-dibromovinyl)benzene (6). The title compound was synthesized using the same method as was **3**; however, **5** was used as the starting material. The compound was used without further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.46 (s, 2 H, $CHBr_2$), 7.56 (s, 4 H, aromatic H's). GC/MS (DIP) *m/z*: 449 (15.04), 448 (7.55), 447 (64.75), 446 (11.37), 445 (100), 444 (4.88), 443 (73.92), 441 (17.19), 288 (2.99), 287 (26.86), 286 (5.39), 285 (53.79), 284 (3.53), 283 (27.99), 206 (2.98), 205 (4.77), 204 (3.45), 203 (4.27), 126 (71.68).

1,3,5-Tris*(*2,2-dibromovinyl)benzene (8). The title compound was synthesized using the same method as was **3**; however, **7** was used as the starting material. The compound was used without further purification. White solid, mp 88−89 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.47 (s, 3 H, $CHBr_2$), 7.65 (s, 3 H, aromatic H's). GC/MS (DIP) *m/z*: 635 (2.75), 634 (2.01), 633 (15.73), 632 (6.73), 631 (34.23), 630 (3.77), 629 (47.67), 628 (9.80), 627 (37.72), 625 (15.70), 473 (5.91), 472 (4.45), 471 (17.51), 470 (2.55), 469 (24.78), 468 (4.23), 467 (22.85), 465 (8.39), 389 (1.78), 388 (5.50), 387 (2.01), 385 (2.11), 311 (16.67), 310 (6.22), 309 (27.23), 150 (69.90), 75 (100).

Bis-1,4-[2,2-**bis(4-dodecyloxyphenyl ethynyl)ethenyl]-benzene (9).** This compound was synthesized according to a modified literature report.[23] 1,4-Bis-*β*,*β*-dibromodistyrene **6** (249 mg, 0.560 mmol) was dissolved in 200 mL of THF/NEt_3 (1:1). $Pd(PPh_3)_2Cl_2$ (78.5 mg, 0.110 mmol), triphenylphosphine (29.3, 0.110 mmol), and CuI (21.3 mg, 0.110 mmol) were then added. The reaction mixture was stirred under argon for 10 min. 1-Ethynyl-4-dodecyloxybenzene **4** (830 mg, 2.68 mmol), dissolved in 5.00 mL of THF, was added slowly through a septum over a period of 1 h to the reaction mixture. The reaction mixture was stirred under argon for 24 h at 70 °C in an oil bath. The reaction mixture was run through a short bed of silica gel using hexanes as eluent and then run through another column using hexanes/CH_2Cl_2 (4:1) as eluent to yield 100 mg (14%) of the title compound (orange solid); mp 68−69 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85−0.91 (t, 12 H, CH_3), 1.19−1.32 (m, 36 H), 1.72−1.85 (pentet, 8 H, OCH_2CH_2), 3.92−4.00 (sextet, 8 H, OCH_2), 6.82−6.88 (dd, 8 H, J_1 = 8.8 Hz, J_2 =3.8 Hz, *o*-H's to OR), 7.08 (s, 2 H, vinyl H's), 7.44−7.50 (dd, 8 H, J_1 = 8.8 Hz, J_2 =1.4 Hz, *m*-H's to OR), 7.98 (s, 4 H, aromatic H's of the benzene core). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.40 (CH_3), 22.98 (CH_2), 26.31 (CH_2), 26.33 (CH_2), 29.49 (CH_2), 29.52 (CH_2), 29.65 (CH_2), 29.69 (CH_2), 29.73 (CH_2), 29.87 (CH_2), 29.89 (CH_2), 29.92 (CH_2), 32.21 (CH_2), 68.35 (C), 68.38 (C), 86.67 (C), 88.67 (C), 89.37 (C), 95.95 (C), 104.56 (C), 114.78 (CH), 114.95 (CH), 114.99 (CH), 115.08 (CH), 129.10 (CH), 133.40 (CH), 136.73 (C), 141.11 (CH), 159.67 (C), 159.94 (C). Anal. Calcd for $C_{90}H_{122}O_4{\cdot}H_2O$: C, 84.06; H, 9.72. Found: C, 84.30; H, 9.79.

Tris-1,3,5-[2,2-bis(4-dodecyloxyphenyl ethynyl)ethenyl]-benzene (10). This compound was synthesized in the same way as was **9**; however, 1,3,5-tris*(*2,2-dibromovinyl)benzene **8** was used as starting material. Compound **10** (60.0 mg, 5%) was isolated; mp 60−61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86−0.90 (m, 18 H, CH_3), 1.26−1.46 (m, 108 H), 1.67−1.74 (pentet, 6 H, OCH_2CH_2), 1.76−1.83 (pentet, 6 H, OCH_2CH_2), 3.85−3.88 (t, 6 H, OCH_2), 3.95−3.99 (t, 6 H, OCH_2), 6.82−6.88 (m, 12 H, *o*-H's to OR), 7.03 (s, 3 H, vinyl H's), 7.46−7.50 (t, 6 H, *m*-H's to OR),7.55−7.57 (d, 6 H, *J* = 8.8 Hz, *m*-H's to OR), 8.11 (s, 1 H, aromatic H of the benzene core), 8.33 (d, 2 H, *J* = 1.2 Hz, aromatic H's of the benzene core). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.12 (CH_3), 22.69 (CH_2), 25.99 (CH_2), 26.03 (CH_2), 29.21 (CH_2),

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29.36 (CH_2), 29.41 (CH_2), 29.43 (CH_2), 29.59 (CH_2), 29.60 (CH_2), 29.64 (CH_2), 29.66 (CH_2), 31.92 (CH_2), 68.02 (C), 68.10 (C), 68.18 (C), 72.84 (C), 74.79 (C), 80.87 (C), 82.08 (C), 86.01 (C), 87.70 (C), 89.19 (C), 96.02 (C), 105.68 (C), 113.34 (C), 113.34 (CH), 114.39 (CH), 114.53 (CH), 114.63 (CH), 114.68 (CH), 114.74 (CH), 122.22 (C), 133.24 (CH), 133.42 (CH), 134.15 (CH), 136.44 (C), 159.48 (C), 159.82 (C), 160.09 (C). Anal. Calcd for $C_{132}H_{180}O_6$: C, 85.11; H, 9.74; O, 5.15. Found: C, 85.26; H, 9.45; O, 4.98.

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Supporting Information Available: The absorption spectra of **9** and **10** in ethyl acetate. This material is available free of charge via the Internet at http://pubs.acs.org.

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