

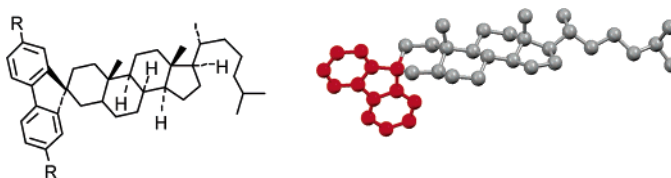
Preparation of Chiral Cholestanofluorene and Its Electron-Rich Derivatives for Isolation of a Stable Cation–Radical Salt

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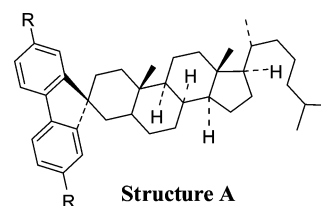


A simple and practical synthesis of a variety of chiral fluorene derivatives is described where a cholestane moiety is attached to the carbon 9 of the fluorene ring system from readily available starting materials. An appropriately substituted fluorene derivative (i.e., R = OMe) forms a highly colored (chiral) cation–radical that can be isolated as robust hexachloroantimonate salt. Interestingly, the simplest cholestanofluorene (i.e., R = H) can also be transformed into a dibromo derivative (i.e., R = Br), a precursor to the (poly)cholestanofluorenes where the cholestane moieties will serve not only as groups that impart chirality but also allow them to be soluble in common organic solvents. The details of these works are described.

Introduction

Poly(9,9-dialkylfluorenes), produced by polymerization of 9,9-dialkylfluorene, are extensively investigated as electroluminescent polymers for a variety of applications in the emerging area of molecular electronics and nanotechnology.^{1,2} Much attention has been focused toward enhancing the processibility and the efficiency of polyfluorenes in functional devices by modifications of the groups attached at the 9 position of the fluorene moiety.^{1,2} Interestingly, an introduction of a readily available (chiral) cholestane unit onto the fluorene moiety (see structure **A**) can not only satisfy the processibility needs owing to the lipophilic nature of the (bio-compatible) cholestane moieties³ but can also impart chirality to the resulting fluorene

derivatives. Moreover, the appropriately substituted cholestanofluorene derivatives and its highly colored cation–radical salts may be potentially useful for the preparation of chiroptical switching devices⁴ as well as chiral liquid crystals.⁵



Accordingly, we now describe a simple and efficient synthesis of hitherto unknown cholestanofluorene (see structure **A**) and its derivatives from the readily available cholestanone as the starting material. Also, the preparation of an electron-rich dimethoxycholestanofluorene derivative allows the isolation of a stable cation–radical salt by 1-electron oxidation, using a variety of oxidants as follows.

(1) (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402. (b) Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2002**, *10*, 1471. (c) Rees, I. D.; Robinson, K. L.; Holmes, A. B.; Towns, C. R.; O'Dell, R. *MRS Bull.* **2002**, *27*, 451. (d) Barbec, J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *14*, 15.

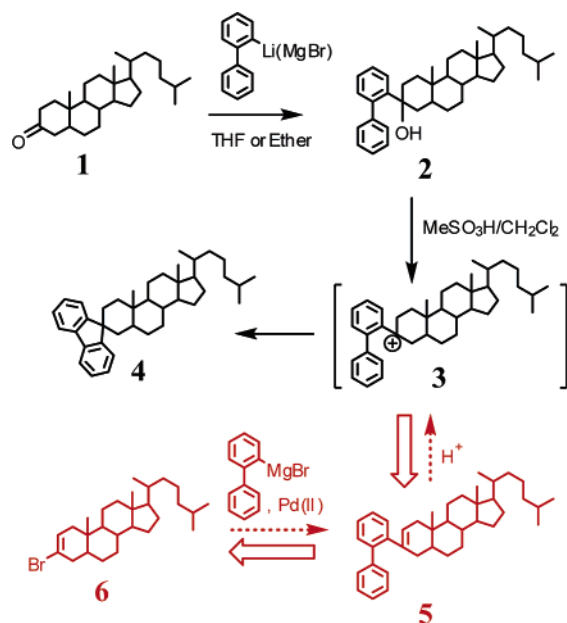
(2) (a) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267. (b) Sonar, P.; Zhang, J.; Grimsdale, A. C.; Müllen, K.; Surin, M.; Lazzaroni, R.; Leclère, P.; Tierney, S.; Heeney, M.; McCulloch, I. *Macromolecules* **2004**, *37*, 709.

(3) For other usage of cholestane framework, see: (a) Yus, M.; Soler, T.; Foubelo, F. *Tetrahedron: Asymmetry* **2001**, *12*, 801. (b) Dogariu, A.; Gupta, R.; Heeger, A. J.; Wang, H. *Synth. Met.* **1999**, *100*, 95. (c) Marcelis, A. T. M.; Koudijs, A.; Sudhoelter, E. J. R. *Liq. Cryst.* **1995**, *18*, 843. (d) Erker, G.; Mollenkopf, C. *J. Organomet. Chem.* **1994**, *483*, 173. (e) Breslow, R.; Wiedenfeld, D. *Tetrahedron Lett.* **1993**, *34*, 1107.

(4) (a) Carreno, M. C.; Garcia, I.; Ribagorda, M.; Merino, E.; Pieraccini, S.; Spada, G. P. *Org. Lett.* **2005**, *7*, 2869. (b) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *Chem. Rev.* **2000**, *100*, 1789. (c) Mori, T.; Inoue, Y. *J. Phys. Chem. A* **2005**, *109*, 2728.

(5) (a) Marcelis, A. T. M.; Koudijs, A.; Sudhoelter, E. J. R. *Liq. Cryst.* **1995**, *18*, 843. (b) Aldred, M. P.; Eastwood, A. J.; Kitney, S. P.; Richards, G. J.; Vlachos, P.; Kelly, S. M.; O'Neill, M. *Liq. Cryst.* **2005**, *32*, 1251 and references cited therein.

SCHEME 1



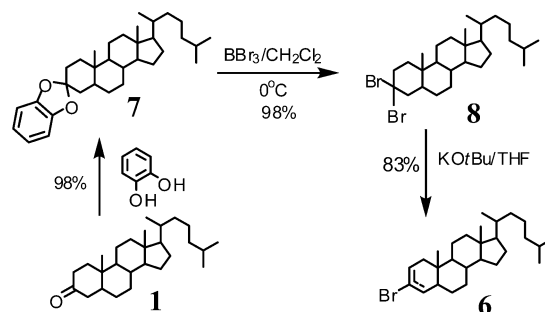
Results and Discussion

Our initial attempt to synthesize the parent cholestanofluorene (**4**) via a direct two-step route (Scheme 1) met with limited success. For example, a reaction of cholestanone (**1**) with either 2-biphenylmagnesium bromide or 2-biphenyllithium afforded at best a ~20% yield of the tertiary alcohol **2**. However, chromatographically purified tertiary alcohol **2** underwent a smooth intramolecular Friedel–Crafts alkylation in dichloromethane in the presence of a catalytic amount of methanesulfonic acid via cationic intermediate **3** to produce cholestanofluorene **4** in quantitative yield. The repeated (failed) attempts to improve the yield of alcohol **2**—a precursor for the cationic intermediate **3**—suggested that an alternative (general) approach was desired for the preparation of **4** and its derivatives. It was envisioned that the same cationic intermediate **3** could also be produced by protonation of an alkene derivative **5**, which may, in turn, be obtained by an efficient palladium-catalyzed coupling⁶ of the 2-biphenylmagnesium bromide with hitherto unknown 3-bromocholestene **6**, i.e., Scheme 1.

Fortunately, employing a simple 3-step sequence⁷ afforded an isomeric mixture of 3-bromocholest-2(3)-enes **6** from commercially available cholestanone in excellent yield without a need for chromatographic purification, i.e., Scheme 2.

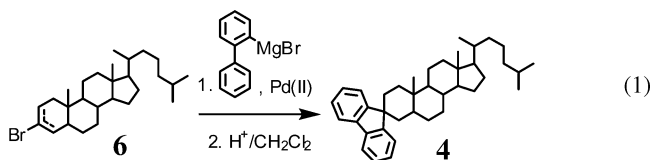
Thus, a reaction of cholestanone (**1**) with catechol in benzene in the presence of an acid catalyst⁸ afforded 1,3 benzodioxole derivative (**7**) quantitatively. A reaction of **7** with boron tribromide in dichloromethane at 0 °C afforded exclusively a gem-dibromo derivative **8** in 98% yield.⁷ A dehydrobromination of the crude **8** in tetrahydrofuran in the presence of potassium *tert*-butoxide afforded roughly an 8:2 isomeric mixture of 3-bromocholest-2(3)-enes **6** in 83% yield. It is noteworthy that

SCHEME 2



all three steps can be easily carried out without a need for chromatographic purification of the intermediates or the final product. Note that the molecular structures of the intermediates **7** and **8** were also confirmed by X-ray crystallography (see the Experimental Section and the Supporting Information for details).

Expectedly, a simple palladium-catalyzed coupling⁶ between the isomeric mixture of bromocholestenes **6** and the biphenylmagnesium bromide in the presence of a catalytic amount of bis(triphenylphosphine)palladium dichloride in refluxing tetrahydrofuran afforded a mixture of 3-biphenylcholestenes **5** in good yield. The ¹H NMR spectrum of the crude material clearly showed that signals due to the olefinic hydrogens of **6** as symmetrical multiples at 5.66 and 5.91 ppm were shifted to 5.30 and 5.53 ppm, respectively. The isomeric mixture of 3-biphenylcholestenes **5** were subjected to Friedel–Crafts cyclization in dichloromethane containing methanesulfonic acid at 0 °C to afford single cholestanofluorene **4** in good overall yield in two steps, i.e., eq 1.



The molecular structure of **4** was established by ¹H/¹³C NMR spectroscopy,^{9a} mass spectrometry, and elemental analysis, and was further confirmed by X-ray crystallography (Figure 1). The molecular geometries of the fluorene as well as of the cholestane moieties in **4** are comparable to those found in 9,9-dimethylfluorene and in various cholestane derivatives, respectively.^{9b} Notably, however, a head-to-tail packing arrangement of **4** in the crystalline state where the H's on the perfectly ordered C17-aliphatic chains of cholestane frameworks make short C–H⋯π contacts (with distances of 2.7–3.0 Å) with both faces of the fluorene rings is uniquely different from other 9,9-dialkylfluorenes (see Figure 1). Such a packing arrangement may prove to be highly beneficial for the device constructions with use of poly(cholestanofluorenes) as opposed to the traditional poly(9,9-dialkylfluorenes) with simple alkyl chains (vide infra).

The versatility of the synthetic strategy in eq 1 allows the preparation of electron-rich 2,7-dimethoxyfluorene derivative

(6) Kumada, K. *Pure Appl. Chem.* **1980**, *52*, 669. Also see: (a) Rathore, R.; Abdelwhaed, S. H.; Guezi, I. A. *J. Am. Chem. Soc.* **2003**, *125*, 8712. (b) Rathore, R.; Deselnicu, M. I.; Burns, C. L. *J. Am. Chem. Soc.* **2002**, *124*, 14832.

(7) Compare: Napolitano, E.; Fiaschi, R.; Mastroilli, E. *Synthesis* **1986**, 122.

(8) Li, T.-S.; Li, L.-J.; Yang, F. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3561.

(9) (a) Note that the two benzenoid rings of the fluorene moiety in **4** show different ¹H/¹³C signals due to the rigidity of cyclohexane framework, which does not allow chair-to-chair interconversions on the NMR time scale. It is expected that the simple spiro[cyclohexane-1,9'-fluorene] will show the presence of the symmetrical fluorene moiety by ¹H/¹³C NMR spectroscopy because it can undergo rapid chair-to-chair interconversions on the NMR time scale, e.g., see: Ohwada, T. *J. Am. Chem. Soc.* **1992**, *114*, 8818. (b) Cambridge Crystallographic Database, 2006.

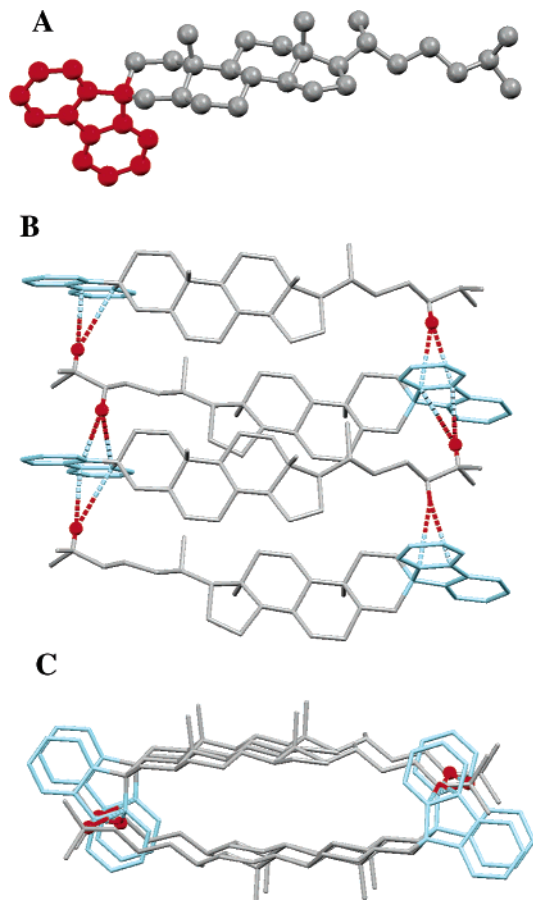
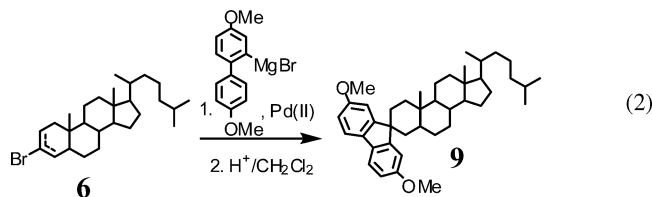


FIGURE 1. The molecular structure of cholestanofluorene **4** (A) and the packing diagrams (B and C) showing the sandwiching of the C17-aliphatic chains of cholestane frameworks due to C–H \cdots π interactions.

for the isolation of (stable) chiral cation–radical salt with ease. For example, a cholestanofluorene derivative with methoxy substituents (i.e., **9**) was easily obtained by a reaction of 4,4'-dimethoxybiphenyl-2-magnesium bromide¹⁰ with bromocholestenes (**6**) in the presence of a catalytic amount of bis-triphenylphosphinepalladium dichloride in tetrahydrofuran followed by cyclization with methanesulfonic acid at 0 °C in 77% isolated yield, i.e., eq 2.



With the dimethoxycholestanofluorene **9** at hand, we first evaluated its electron-donor strength and the initial indication of the cation radical stability by cyclic voltammetry. Thus, donor **9** was subjected to electrochemical oxidation at a platinum electrode as a 2.5×10^{-3} M solution in dichloromethane containing 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte. The cyclic voltammograms of **9** consistently met the reversibility criteria at various scan rates of 25–400 mV s⁻¹ (see Figure 2),

(10) Sparling, J.; Fung, D.; Safe, S. *Biomed. Mass Spectrom.* **1980**, *7*, 13.

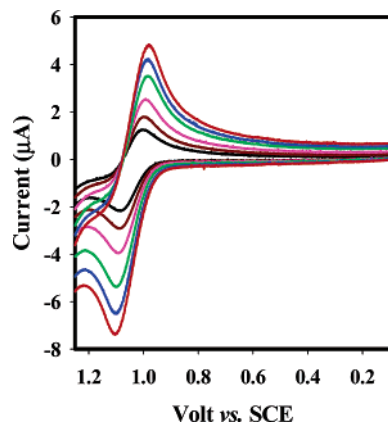


FIGURE 2. Cyclic voltammograms of 2.5 mM dimethoxycholestanofluorene **9** in CH₂Cl₂ containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate at a scan rate of 25–400 mV s⁻¹ at 22 °C.

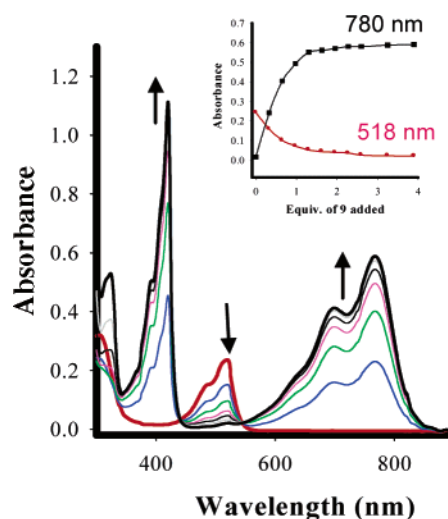


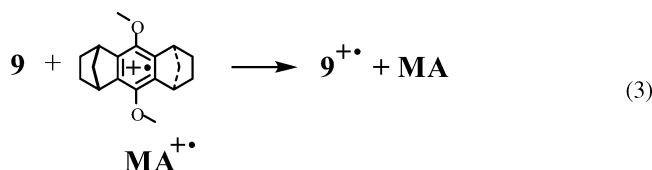
FIGURE 3. Spectral changes upon the reduction of 3.1×10^{-5} M MA^{+•} (red) by incremental addition of 1.9×10^{-3} M **9** to **9**^{+•} in dichloromethane at 22 °C. Inset: A plot of depletion of absorbance of MA^{+•} (circles, monitored at 518 nm) and an increase of the absorbance of **9**^{+•} (squares, monitored at 780 nm) against the equivalent of added **9**.

as they all showed cathodic/anodic peak current ratios of $i_a/i_c = 1.0$ (theoretical) as well as the differences between anodic and cathodic peak potentials of $p_a - p_c \approx 70$ mV at 22 °C. A quantitative evaluation of the CV peak current with added ferrocene (as an internal standard) revealed that the oxidation potential of **9** ($E_{ox} = 1.08$ V vs SCE) was significantly lower than the (irreversible) redox potential ($E_{ox} = 1.71$ V) for the parent cholestanofluorene **4**.

The electrochemical reversibility of **9** and its relatively low oxidation potential prompted us to carry out its oxidation to the corresponding cation radical using a stable cation–radical salt MA^{+•} SbCl₆⁻ as an aromatic oxidant ($E_{red} = 1.11$ V vs SCE).¹¹ Thus, Figure 3 shows the spectral changes attendant upon the reduction of 3.1×10^{-5} M MA^{+•} [$\lambda_{max}(\log \epsilon) = 518$ nm (3.86)] by incremental additions of 1.9×10^{-3} M at 22 °C in dichloromethane. The presence of well-defined isosbestic points at $\lambda_{max} = 443$ and 544 nm in Figure 3 are indicative of the uncluttered character of the electron transfer. Furthermore,

(11) Rathore, R.; Burns, C. L.; Deselnicu, M. I. *Org. Synth.* **2005**, *82*, 1.

a plot of the depletion of $\text{MA}^{+\bullet}$ (i.e., decrease in the absorbance at 518 nm) and formation of $\mathbf{9}^{+\bullet}$ (i.e., increase in the absorbance at 780 nm) against the increments of added $\mathbf{9}$ (inset, Figure 3) established that $\text{MA}^{+\bullet}$ was completely consumed after the addition of 1 equiv of $\mathbf{9}$; and the resulting absorption spectrum of the green $\mathbf{9}^{+\bullet}$ [$\lambda_{\text{max}} = 420, 700, \text{ and } 768 \text{ nm}$] remained unchanged upon further addition of neutral $\mathbf{9}$, i.e., eq 3.



It is noteworthy that the green $\mathbf{9}^{+\bullet}$ obtained in eq 3 is highly persistent at room temperature and did not show any decomposition during a 12 h period at 22 °C. The high stability of the $\mathbf{9}^{+\bullet}$ allowed the isolation of its crystalline salt as follows. Thus, a treatment of a solution of $\mathbf{9}$ with nitrosonium hexachloroantimonate ($\text{NO}^+\text{SbCl}_6^-$) in anhydrous dichloromethane at 0 °C immediately resulted in a dark green solution (vide infra) from which the microcrystalline salt [$\mathbf{9}^{+\bullet}\text{SbCl}_6^-$] was isolated, by precipitation with hexanes, in nearly quantitative yield according to the stoichiometry in eq 4.¹²



The highly colored $\mathbf{9}^{+\bullet}\text{SbCl}_6^-$ salt obtained in eq 4 was found to be extremely robust and can be recrystallized from a dichloromethane solution by a slow diffusion of toluene at -20 °C. Unfortunately, however, repeated attempts to obtain single crystals suitable for X-ray crystallography of [$\mathbf{9}^{+\bullet}\text{SbCl}_6^-$] were thus far unsuccessful.

In summary, we have presented a facile approach for the synthesis of chiral cholestanofluorenes from readily available starting materials and have shown that its methoxy derivative $\mathbf{9}$ forms a stable cation–radical salt—a potentially important material for the applications in the area of chiroptical switching devices.⁴ Moreover, parent cholestanofluorene $\mathbf{4}$ can be easily derivatized by electrophilic substitution reactions at 2,7-positions, i.e., a reaction of $\mathbf{4}$ with *tert*-butyl chloride in dichloromethane containing a catalytic amount of ferric chloride afforded 2,7-di-*tert*-butyl derivative $\mathbf{10}$ in 92% yield¹³ (Scheme 3), whereas a bromination reaction produces the corresponding dibromo derivative $\mathbf{11}$ in 97% yield, i.e., Scheme 3.

The availability of dibromo derivative $\mathbf{11}$ will allow its ready transformation to the chiral poly(cholestanofluorenes) with standard palladium or nickel catalysts.¹⁴ The poly(cholestanofluorenes) can also be accessed via anodic oxidation of parent $\mathbf{4}$.¹⁵ These works are being pursued actively.

Experimental Section

Cholestanone was prepared according to a literature procedure.¹⁶ Nitrosonium hexachloroantimonate was prepared from a reaction of SbCl_5 and NOCl in dichloromethane at -78 °C and the resulting

(12) Rathore, R.; Kumar, A. S.; Lindeman, S. V.; Kochi, J. K. *J. Org. Chem.* **1998**, *63*, 5847 and references cited therein.

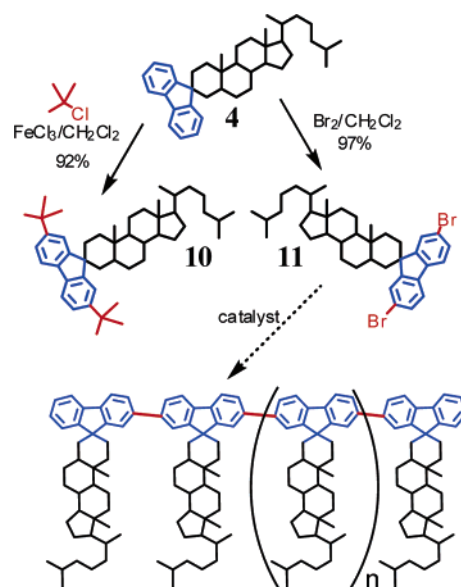
(13) Rathore, R.; Burns, C. L. *J. Org. Chem.* **2003**, *68*, 4071.

(14) Setayesh, S.; Marsitzky, D.; Muellen, K. *Macromolecules* **2000**, *33*, 2016 and references cited therein.

(15) Rault-Berthelot, J.; Simonet, J. *J. Electroanal. Chem.* **1985**, *182*, 187.

(16) Bruce, W. F. *Organic Syntheses*; Wiley: New York; Collect. Vol. 2, p 139; Vol. 17, p 43.

SCHEME 3



salt was recrystallized from a dichloromethane–hexanes mixture and stored in an inert-atmosphere glovebox.¹³ (See the Supporting Information for a General Experimental Section.)

Spiro[1,3-benzodioxole-2,3'-cholestane] (7). The ketal $\mathbf{7}$ was synthesized by a reaction of cholestanone (9.4 g, 24.4 mmol) with catechol (7.8 g, 70.8 mmol) according to a slightly modified literature procedure.⁸ Thus, after completion of the reaction, the catalyst was removed by filtration through a pad of celite and the pad was washed further with ether (3 × 50 mL). The solvent was removed in vacuo and the resulting residue was dissolved in dichloromethane (200 mL) and washed successively with 10% potassium hydroxide, water, and brine, then dried over anhydrous magnesium sulfate. Evaporation of the solvent afforded $\mathbf{7}$ as a white solid in nearly quantitative yield (11.4 g, 98%): mp 155–156 °C (lit.⁸ mp 155–156 °C); ¹H NMR (CDCl_3) δ 0.67–2.07 (m, 46H, cholestanone framework protons), 6.70–6.79 (m, 4H); ¹³C NMR (CDCl_3) δ 11.7, 12.3, 18.9, 21.5, 22.8, 23.1, 24.1, 24.5, 28.2, 28.5, 28.6, 31.5, 32.0, 35.4, 35.7, 36.1, 36.4, 38.1, 39.7, 40.2, 42.8, 42.9, 53.9, 56.4, 56.6, 108.4, 108.6, 118.5, 121.0, 147.3, 147.5; GC-MS m/z 478 (M^+), 478 calcd for $\text{C}_{33}\text{H}_{50}\text{O}_2$. Note that the white solid, obtained above, was sufficiently pure and used in the next step without further purification. Moreover, an excellent quality of single crystals were obtained by a simple crystallization from a mixture of dichloromethane–acetonitrile and were further characterized by X-ray crystallography (see the Supporting Information).

3,3-Dibromocholestanone (8).⁷ To a stirred solution of $\mathbf{7}$ (8.9 g, 18.6 mmol) in dichloromethane (40 mL) at 0 °C was added dropwise a 1 M solution of boron tribromide in dichloromethane (23 mL, 23 mmol) under an argon atmosphere and the resulting mixture was stirred for 12 h while maintaining the temperature at 0 °C. The reaction was quenched with ice-cold water (50 mL) and the dichloromethane layer was separated. The aqueous layer was extracted with dichloromethane (3 × 25 mL). The combined organic extracts were washed successively with water (50 mL), 10% sodium hydroxide (2 × 25 mL), and water (50 mL), then dried over anhydrous magnesium sulfate. Recrystallization of the resulting crude solid from a mixture of dichloromethane/acetonitrile afforded $\mathbf{8}$ as a white solid in nearly quantitative yield (9.7 g, 98%): mp 150–151 °C ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$); ¹H NMR (CDCl_3) δ 0.61–2.60 (m, 46H, cholestanone framework protons); ¹³C NMR (CDCl_3) δ 12.2, 12.7, 18.8, 21.2, 22.7, 23.0, 24.0, 24.3, 27.4, 28.2, 28.4, 31.8, 35.5, 35.7, 36.0, 36.3, 37.4, 39.7, 40.4, 42.8, 44.9, 46.2, 52.0, 53.8, 56.4, 56.5, 72.1. Anal. Calcd for $\text{C}_{27}\text{H}_{46}\text{Br}_2$: C, 61.13; H, 8.74. Found: C, 61.24; H, 8.65. HRMS (m/z) calcd for $\text{C}_{27}\text{H}_{46}\text{Br}_2$ 528.1972, found 528.1966. Also note that single crystals of $\mathbf{8}$ were obtained by

crystallization from a mixture of dichloromethane–acetonitrile and were characterized by X-ray crystallography (see the Supporting Information).

3-Bromocholestenes (6). To a magnetically stirred solution of **8** (8.8 g, 16.7 mmol) in anhydrous tetrahydrofuran (50 mL) was added excess potassium *tert*-butoxide (3.4 g, 30 mmol). The resulting mixture was stirred under an argon atmosphere for 3 h at room temperature. The reaction was quenched with saturated ammonium chloride solution (50 mL) and triturated with dichloromethane (100 mL). The organic layer was separated and the aqueous layer was further extracted with dichloromethane (3 × 25 mL). Combined organic extracts were washed with water (3 × 25 mL) and brine (3 × 25 mL), then dried over anhydrous magnesium sulfate. Evaporation of the solvent and crystallization of the resulting solid from a mixture of dichloromethane and methanol afforded **6** as a colorless solid (6.2 g, 83%): mp 88–89 °C (CH₂Cl₂/CH₃-OH); ¹H NMR (CDCl₃) δ 5.91 and 5.66 (sym m's, 1H), 0.59–2.48 (m, 44H, cholestane framework protons); ¹³C NMR (CDCl₃) δ 12.0, 12.1, 12.3, 18.8 (s), 18.9, 21.2, 21.5 (s), 22.7, 23.0, 24.0, 24.3 (s), 24.4, 27.4 (s), 28.2, 28.42, 28.45 (s), 31.7, 32.0 (s), 33.6 (s), 34.2, 34.9 (s), 35.65 (s), 35.68, 36.0, 36.3, 36.5 (s), 39.7, 40.08, 40.10, 40.16 (s), 42.2, 42.67 (s), 42.68, 42.9 (s), 43.8, 48.8 (s), 52.9 (s), 53.7, 56.4, 56.53, 56.57 (s), 120.6, 121.2 (s), 127.7, 133.2 (s). Note that "(s)" refers to the signals arising from ~20% of the isomeric **6**. Anal. Calcd for C₂₇H₄₅Br: C, 72.14; H, 10.09. Found: C, 72.13; H, 10.10. HRMS (*m/z*) calcd for C₂₇H₄₅Br 448.2700, found 448.2705.

Cholestanofluorene (4). A freshly prepared solution of 2-biphenylmagnesium bromide [from 2-bromobiphenyl (2.3 mL, 13.4 mmol) and excess magnesium turnings (1.3 g, 53.4 mmol) in anhydrous tetrahydrofuran (80 mL)] was transferred to a Schlenk flask containing **6** (4.0 g, 8.9 mmol) and a catalytic amount of bis-(triphenylphosphine)palladium dichloride (0.25 g) with the aid of a canula under an argon atmosphere and at 22 °C. The resulting yellow mixture was refluxed for 24 h, cooled to room temperature, and quenched with saturated ammonium chloride solution (50 mL). The aqueous layer was extracted with dichloromethane (3 × 50 mL) and the combined organic extracts were dried over anhydrous magnesium sulfate and filtered. Evaporation of the solvent in vacuo afforded crude **5** as a yellow solid that was used in the next step without purification. ¹H NMR (400 MHz, CDCl₃) δ 2.02–0.61 (m, 44H, cholestane framework protons), 5.53 and 5.30 (sym m, 1H) due to a single olefinic proton from two isomers, 7.61–6.99 (m, 9H).

To a solution of the isomeric mixture of biphenylcholestenes **5**, from above, in anhydrous dichloromethane (50 mL) was added dropwise methanesulfonic acid (2 mL) under an argon atmosphere and at 0 °C. The ice bath was removed and the resulting yellow solution was stirred for 1 h at 22 °C. The reaction mixture was quenched with aqueous sodium carbonate solution (50 mL) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 50 mL) and the combined organic extracts were dried over anhydrous magnesium sulfate and filtered through a short celite pad. Evaporation of the solvent and crystallization of the resulting solid from a mixture of dichloromethane/acetonitrile afforded **4** as a white crystalline solid (2.7 g, 60%): mp 181–182 °C (CH₂Cl₂/CH₃CN); ¹H NMR (CDCl₃) δ 0.72–2.32 (m, 46H, cholestane framework protons), 7.28–7.47 (m, 5H), 7.69–7.72 (m, 1H), 7.76 (d, *J* = 7, 1H), 7.90 (d, *J* = 7, 1H); ¹³C NMR (CDCl₃) δ 12.1, 12.3, 18.9, 21.3, 22.8, 23.1, 24.1, 24.4, 28.2, 28.5, 29.0, 31.2, 32.2, 35.5, 35.8, 35.9, 36.0, 36.4, 38.5, 39.7, 40.3, 42.6, 42.8, 50.92, 55.1, 56.5, 56.8, 119.7, 120.2, 123.0, 125.6, 126.6, 127.04, 127.08, 127.5, 139.3, 140.1, 153.3, 154.3. Anal. Calcd for C₃₉H₅₄: C, 89.59; H, 10.41. Found: C, 89.49; H, 10.52. HRMS (*m/z*) calcd for C₃₉H₅₄ 522.4231, found 522.4226.

2,7-Dimethoxycholestanofluorene (9). Following a similar procedure, as above, a reaction of 4,4'-dimethoxy-2-biphenylmagnesium bromide [from 4,4'-dimethoxy-2-bromobiphenyl¹⁰ (1.8 g, 6.2 mmol) in anhydrous tetrahydrofuran (45 mL)] with **6** (1.84 g, 4.1 mmol) in the presence of a catalytic amount of bis-(triphenylphosphine)palladium dichloride (0.12 g) followed by a reaction with methanesulfonic acid (1 mL) in dichloromethane (50 mL) afforded **9**, which was purified by column chromatography with use of hexanes–ethyl acetate as eluent. Recrystallization from a mixture of dichloromethane and acetonitrile afforded **9** as a white solid (1.8 g, 77%): mp 212–213 °C (CH₂Cl₂/CH₃CN); ¹H NMR (CDCl₃) δ 0.70–2.22 (m, 46H, cholestane framework protons), 3.87 (s, 3H), 3.88 (s, 3H), 6.82–6.94 (m, 3H), 7.42–7.57 (m, 3H); ¹³C NMR (CDCl₃) δ 12.0, 12.3, 18.9, 21.2, 22.8, 23.0, 24.1, 24.4, 28.2, 28.5, 28.9, 31.4, 32.1, 35.3, 35.81, 35.85, 36.0, 36.4, 38.7, 39.7, 40.2, 42.3, 42.8, 50.7, 54.9, 55.7, 56.5, 56.7, 109.2, 110.7, 112.3, 113.5, 119.64, 119.67, 132.2, 133.1, 154.6, 155.7, 158.0, 159.2. Anal. Calcd for C₄₁H₅₈O₂: C, 84.48; H, 10.03. Found: C, 84.08; H, 10.02. HRMS (*m/z*) calcd for C₄₁H₅₈O₂ 582.4438, found 582.4437.

2,7-Di-*tert*-butylcholestanofluorene (10). Parent cholestanofluorene **4** (0.52 g, 1.0 mmol) was readily transformed to 2,7-di-*tert*-butylcholestanofluorene (**10**) from a reaction of **4** with *tert*-butyl chloride (0.32 mL, 3 mmol) in anhydrous dichloromethane (25 mL) in the presence of a catalytic amount of ferric chloride (25 mg) with use of a standard literature procedure.¹³ Recrystallization of the resulting crude solid from a mixture of dichloromethane and acetonitrile afforded **10** as a white solid (0.58 g, 92%): mp 168–169 °C; ¹H NMR (CDCl₃) δ 0.72–2.36 (m, 64H, cholestane framework and *tert*-butyl protons), 7.32–7.40 (m, 3H), 7.56–7.63 (m, 2H), 7.90 (s, 1H); ¹³C NMR (CDCl₃) δ 12.3, 12.4, 18.9, 21.4, 22.8, 23.1, 24.0, 24.4, 28.2, 28.5, 29.0, 31.4, 31.9, 32.6, 35.0, 35.1, 35.8, 35.9, 36.01, 36.04, 36.4, 38.8, 39.8, 40.3, 42.8, 42.9, 50.9, 55.9, 56.4, 56.9, 118.9, 119.2, 119.5, 122.6, 123.9, 124.1, 136.8, 137.4, 148.9, 150.2, 153.2, 154.1. Anal. Calcd for C₄₇H₇₀: C, 88.89; H, 11.11. Found: C, 88.57; H, 10.97. HRMS (*m/z*) calcd for C₄₇H₇₀ 634.5472, found 634.5478.

2,7-Dibromocholestanofluorene (11). Parent cholestanofluorene **4** (0.52 g, 1.0 mmol) was readily transformed to 2,7-dibromocholestanofluorene (**11**) from a reaction of **4** with bromine (0.48 g, 3 mmol) in dichloromethane (25 mL) at 22 °C with use of standard procedures. Yield: 0.66 g, 97%; mp 198–199 °C; ¹H NMR (CDCl₃) δ 0.71–2.23 (m, 46H, cholestane framework protons), 7.42–7.58 (m, 5H), 7.95 (d, 1H); ¹³C NMR (CDCl₃) δ 12.0, 12.3, 18.9, 21.2, 22.8, 23.0, 24.0, 24.3, 28.2, 28.4, 28.8, 30.9, 32.0, 35.3, 35.8, 36.0, 36.4, 38.1, 39.7, 40.1, 42.6, 42.8, 51.3, 54.8, 56.5, 56.6, 120.9, 121.1, 121.5, 121.7, 126.5, 128.7, 130.4, 137.2, 138.0, 154.8, 156.1. Anal. Calcd for C₃₉H₅₂Br₂: C, 68.82; H, 7.70. Found: C, 68.53; H, 7.61. HRMS (*m/z*) calcd for C₃₉H₅₂Br₂ 678.2438, found 678.2436.

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Supporting Information Available: General experimental methods, ¹H/¹³C NMR spectra of various compounds, and the ORTEP diagrams and the X-ray crystallographic data for **4**, **7**, and **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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