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CHEMISTRY

Synthesis of New Symmetrical Carbazole- and Fluorene-Containing α-Diketones

M. L. Keshtov[a], S. N. Osipov[a], M. A. Topchiy[a], M. A. Zotova[a], I. O. Konstantinov[a], M. M. Krayushkin[b], S. A. Kuklin[a], and Academician A. R. Khokhlov[a]

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Abstract—A simple and convenient one-step method for the preparation of symmetrical α-diketones has been proposed. The latter are intended to be used in synthesis of new carbazole- and fluorene-containing quinoxalines showing electroluminescent and photovoltaic properties.

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In the last decade, semiconducting organic materials based on carbazole- and fluorene-containing quinoxalines have attracted large attention of researchers. These quinoxaline derivatives are promising building blocks due to their donor–acceptor structure that facilitates charge carrier transport in a semiconductor and improves their mobility balance. These properties of quinoxaline-containing materials favor their application in organic semiconductors [1], light-emitting diodes [2], and photovoltaic devices [3]. Arylquinoxalines are obtained from α-diketone precursors [4, 5]. The latter are also widely used in fine organic synthesis for preparing heterocyclic compounds and pharmaceuticals of different classes [6], as corrosion inhibitors [7], and photosensitive materials [8]. In spite of the wide spectrum of application, there are a few simple and efficient methods for the synthesis of α-diketones [9, 10].

Usually, α-diketones are obtained by the oxidation of benzoins or hydroxybenzoins in the presence of an excess of inorganic oxidizing agents. Although this method is still widely used, it has a number of drawbacks, such as pollution of the environment and low availability of functionalized benzoins [11, 12]. In recent time, the most popular method of synthesis of α-diketones is based on the direct oxidation of internal alkynes obtained in four stages from aromatic bromides and arylacetylenes [13, 14]. Nonetheless, this method also has a number of drawbacks, such as a large number of steps and toxicity and high cost of initial reagents, which make its application more complex.

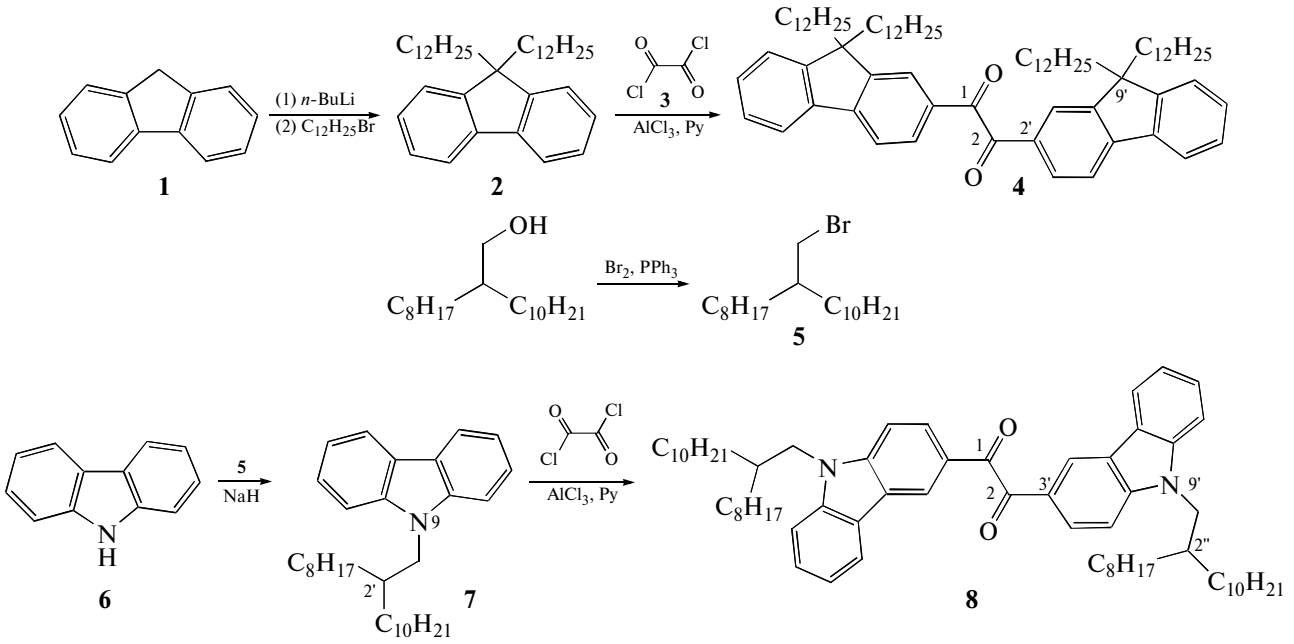
Recently, Krayushkin and co-workers reported the preparation of α-diketones through direct acylation of thiophene derivatives with oxalyl chloride in the presence of aluminum chloride [15]. These results prompted us to prepare two novel symmetrical carbazole- and fluorene-containing α-diketones in good yields by the direct acylation of fluorene and carbazole derivatives with oxalyl chloride in the presence of aluminum chloride according to Scheme 1. In this paper, we propose a simple and convenient one-step method of preparation of symmetrical α-diketones, which will be further used in the synthesis of carbazole- and fluorene-containing functional compounds showing electroluminescent and photovoltaic properties.

1,2-Bis(9',9'-didodecyl-9'H-fluoren-2'-yl)ethane-1,2-dione (**4**) was obtained according to Scheme 1 in two steps from fluorene (**1**). These steps included the lithiation of fluorene followed by the addition of dodecyl bromide to give 9,9-didodecylfluorene (**2**) and the acylation of compound **2** with oxalyl chloride in the presence of aluminum chloride and pyridine to produce α-diketone in 36% yield.

1,2-Bis(9'-(2"-octyldodecyl)carbazol-3'-yl)ethane-1,2-dione (**8**) was obtained also in two steps via the reaction of carbazole (**6**) with 1-bromo-2-octyldodecane (**5**) in the presence of sodium hydride to yield 9-(2'-octyldodecyl)-9H-carbazole (**7**), which was further acylated with oxalyl chloride in the presence of aluminum chloride and pyridine to give α-diketone in 98% yield.

The composition and structure of the intermediate compounds and target products **4** and **8** were con-

[a] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia*
[b] *Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Leninskii pr. 47, Moscow, 119991 Russia*
e-mail: ineos-50@mail.ru



Scheme 1.

firmed by the data of elemental analysis as well as IR and ^{1}H and ^{13}C NMR spectroscopy.

In particular, the ^{1}H NMR spectrum of compound **4** shows three doublets and one triplet in the downfield region at 8.10, 7.90, 7.76, and 7.45–7.35 ppm corresponding to 14 different aromatic hydrogen atoms. The upfield region contains a signal at 2.00 ppm typical for the CH_2 group adjacent to the fluorene ring; the signals of other hydrogen atoms of alkyl chains in compound **4** appear in the range 1.17–0.60 ppm. Although the ^{1}H NMR spectrum of compound **4** is complex, the integrated intensity ratio of the aromatic portion to the aliphatic part corresponds to the supposed structure (Fig. 1a).

The ^{13}C NMR spectrum of compound **4** display 12 signals in the downfield region at 195.3 ppm and in the range 153–118 ppm, which belong to 12 different aromatic carbon atoms, signal typical for the C–O group of compound **4** appears at 195.3 ppm. The upfield region contains signals at 55.3 and 14.3 ppm typical for the cyclopentane moiety of fluorene and the terminal CH_3 group of the alkyl chain. Signals related to other aliphatic carbon atoms appear within 40.4–22.8 ppm, which also confirms the supposed structure (Fig. 1b).

The ^{1}H NMR spectrum of the compound **8** in the downfield range 8.90–7.20 ppm shows one singlet, two doublets, and two multiplets that arise from 14 aromatic protons of the carbazole moiety. The upfield region contains one doublet and one triplet at 4.19 and 0.91 ppm, respectively, typical for the CH_2 group directly bonded to the nitrogen atom and the terminal CH_3 group of the alkyl chain, respectively. Signals from other 66 protons of the alkyl chain appear in the range 2.3–1.16 ppm (Fig. 2a). Although the proton spectrum of compound **8** is complex, the integral intensity ratio of aromatic portion to aliphatic part corresponds to the supposed structure.

The downfield region of ^{13}C NMR spectrum of compound **8** shows 12 signals in the range 150–105 ppm from 12 different aromatic carbon atoms and a signal at 195.2 ppm from the C–O group of α-diketone. The upfield region contains signals at 48.06, 14.12, and 14.10 ppm typical for the CH_2 group directly bonded to the nitrogen atom and the terminal CH_3 group of the alkyl chain. The spectrum shows signals related to other aliphatic carbon atoms in the range 40.4–22.8 ppm, which additionally confirms the supposed structure (Fig. 2b).

EXPERIMENTAL

9,9-Didodecylfluorene (2). A 2.45 M solution of *n*-butyllithium (17.2 mL, 0.042 mol, 2.1 equiv.) in hexane was added to a solution of 3.32 g (0.02 mol) of fluorene in 50 mL of anhydrous THF cooled to –50°C. The reaction mixture was stirred for 15 min, and then 11 mL (11.45 g, 0.046 mol, 2.3 equiv.) of dodecyl bromide was added dropwise. The reaction mixture was heated to ambient temperature and stirred for 2 h until complete discoloration, 100 mL of water was added, and the mixture was extracted with petroleum ether (3 × 25 mL). The organic phase was washed with 20 mL

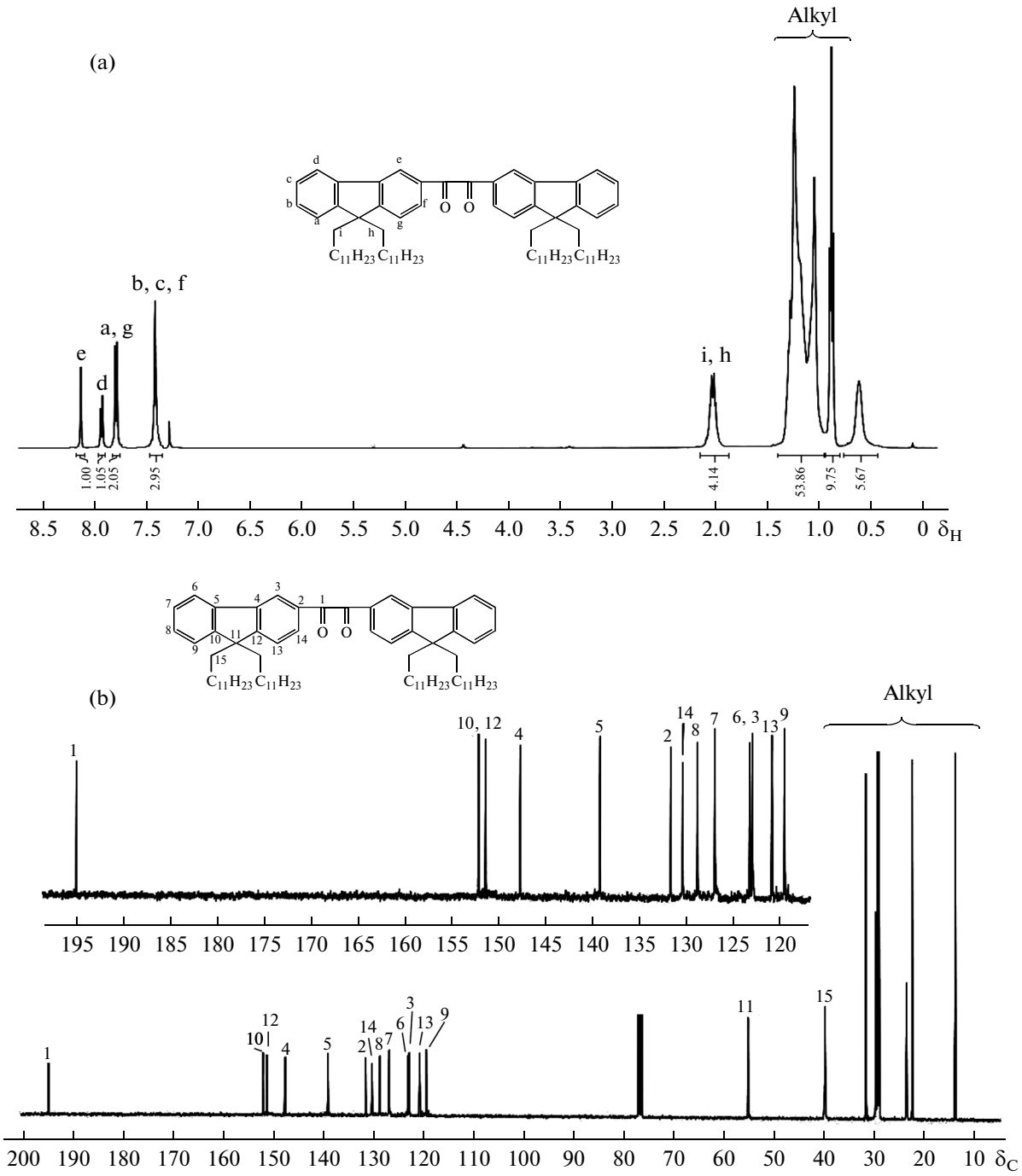


Fig. 1. (a) ^{1}H and (b) ^{13}C NMR spectra of 1,2-bis(9',9'-didodecyl-9'H-fluoren-2'-yl)ethane-1,2-dione (**4**).

of water, dried with $MgSO_4$, and concentrated in a vacuum. Excess dodecyl bromide and byproducts were distilled off from the residue in vacuum (200°C, 0.05 mmHg) to give 9.0 g (89%) of viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.74–7.67 (m, 2H), 7.37–7.27 (m, 6H), 2.01–1.91 (m, 4H), 1.35–0.99 (m, 40H), 0.88 (t, $J = 6.8$ Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 150.8, 141.3, 127.1, 126.8, 123.0, 119.8, 77.5, 77.2, 76.8, 55.1, 40.5, 32.1, 30.2, 29.8, 29.7, 29.5, 29.4, 23.9, 22.8, 14.3.

1,2-Bis(9',9'-didodecyl-9'H-fluoren-2'-yl)ethane-1,2-dione (4). Aluminum chloride (0.6 g, 4.5 mmol) and 3 mL of anhydrous 1,2-dichloroethane were added into a 100-mL three-necked flask equipped with a magnetic stirrer, thermometer, and dropping funnel. The resultant suspension was cooled to –20°C, and a solution of 0.08 mL (0.127 g, 1 mmol) of oxalyl

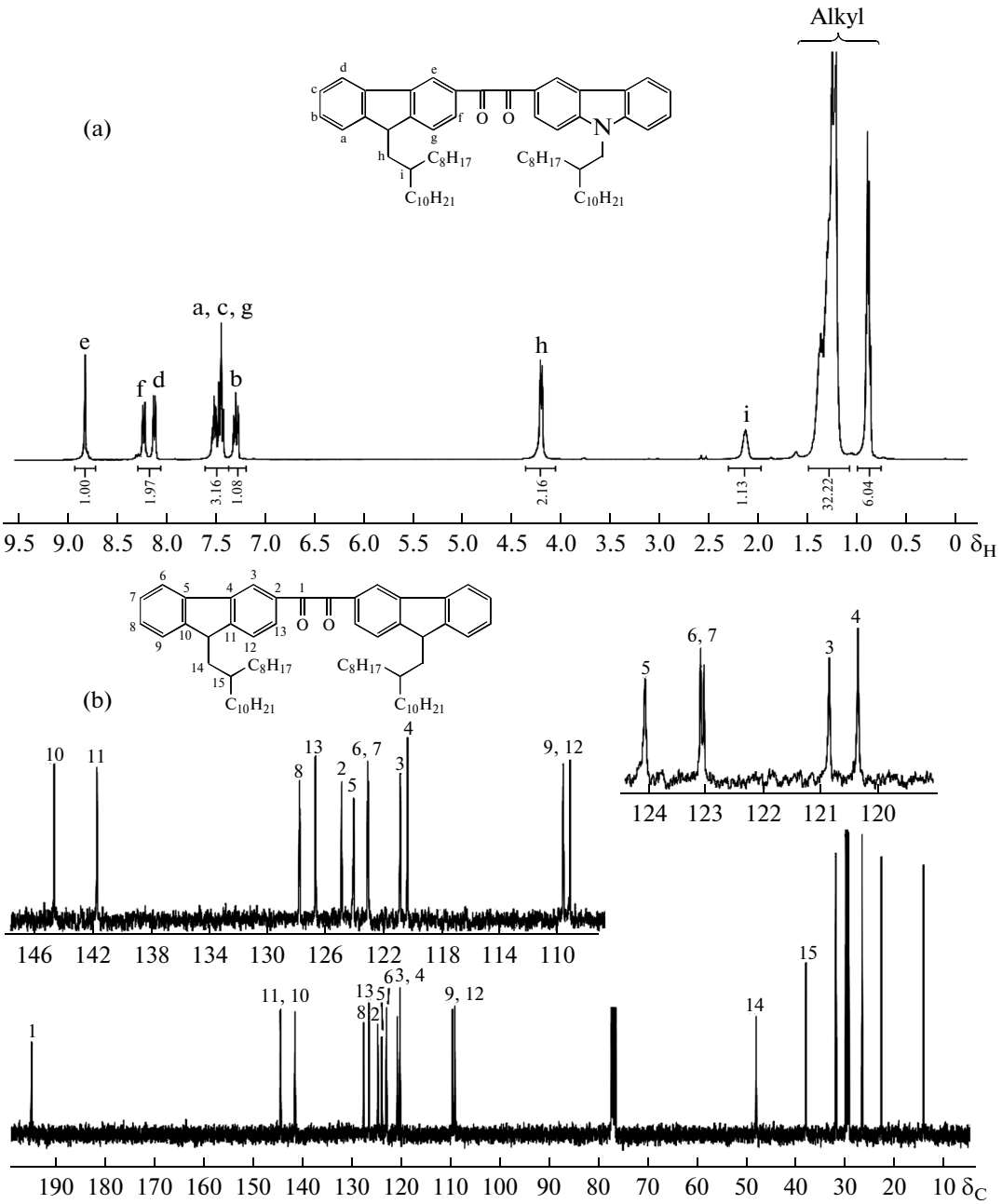


Fig. 2. (a) ^{1}H and (b) ^{13}C NMR spectra of 1,2-bis(9'-(2"-octyldodecyl)carbazol-3'-yl)ethane-1,2-dione (**8**).

chloride in 0.5 mL of anhydrous 1,2-dichloroethane was added dropwise, the mixture was stirred for 5 min, and then a solution of 1 g (2 mmol) of 9,9-didodecylfluorene (**2**) in 0.16 mL (0.16 g, 1.96 mmol) of dry pyridine and 0.5 mL of anhydrous 1,2-dichloroethane was added dropwise. The reaction mixture was stirred for 20 min at −20°C, allowed to warm to 0°C, poured into 100 g of crushed ice, and extracted with dichloromethane (3 × 50 mL). The organic extract was washed with water until the pH of washings became neutral, dried with $MgSO_4$, and concentrated in a vacuum. The residue was purified by column chromatography with gradient elution (petroleum ether (PE), next PE : CH_2Cl_2 = 5 : 1) to give 0.38 g (36%) of viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.09 (s, 2H), 7.89 (dd, J = 7.9, 1.1 Hz, 2H), 7.76 (d, J = 7.8 Hz, 4H), 7.44–7.33 (m, 6H), 2.08–1,94 (m, 8H), 1.32–1.00 (m, 80H), 0.87 (t, J = 6.8 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 195.3, 152.5, 151.7, 148.0, 139.5, 132.0, 130.7, 129.2, 127.3, 123.6, 123.3, 121.2, 119.9, 77.5, 77.2, 76.8, 55.6, 40.3, 32.1, 30.1, 29.8, 29.7, 29.5, 29.4, 24.0, 22.8, 14.3.

For $C_{76}H_{114}O_2$ anal. calcd. (%): C, 86.14; H, 10.84.

Found (%): C, 86.02; H, 10.63.

1-Bromo-2-octyldodecane (5). A 500-mL three-necked flask equipped with magnetic stirrer, septum, and thermometer was filled with argon. Triphenylphosphine (33.4 g, 0.127 mol, 1 equiv.) and 200 mL of anhydrous dichloromethane were placed into the flask. The solution was cooled to 0°C, and 6.52 mL (20.34 g, 0.127 mol, 1 equiv.) of bromine was added dropwise so that the temperature of the reaction mixture was not higher 5°C. After bromine addition was completed, the reaction mixture was stirred for 15 min at 0°C, 45.36 mL (38.0 g, 0.127 mol, 1 equiv.) of 2-octyl-1-dodecanol was added. The reaction mixture was stirred for 12 h at ambient temperature, concentrated in a vacuum, the resultant suspension was diluted with 100 mL of petroleum ether, and filtered. The filtrate was passed through a thin layer of silica gel, washed with petroleum ether, and concentrated in a vacuum to give 43.61 g (95%) of viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.47 (d, J = 4.7 Hz, 2H), 1.66–1.54 (m, 1H), 1.45–1.17 (m, 32H), 0.91 (t, J = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 39.7, 39.5, 32.5, 31.9, 29.8, 29.6, 29.6, 29.5, 29.3, 29.3, 26.5, 22.6, 14.1.

9-(2'-Octyldodecyl)-9H-carbazole (7). Carbazole (5 g, 30 mmol) was dissolved in 50 mL of DMF under an argon atmosphere and then 1.67 g (1.4 equiv.) of 60% sodium hydride suspension in mineral oil was added. After all sodium hydride was added, the reaction mixture was stirred for 20 min, and then, 11 g (30 mmol) of 1-bromo-2-octyldodecane (**5**) was added in one portion in an argon counterflow. The reaction mixture was stirred for 72 h, poured into water, and extracted with petroleum ether. The organic extract was dried with $MgSO_4$, the solvent was removed in a vacuum. The residue was chromatographed in petroleum ether to give 10.3 g (76%) of viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.13 (d, J = 7.7 Hz, 2H), 7.58–7.34 (m, 4H), 7.29–7.24 (m, 2H), 4.19 (d, 2H), 2.20–2.15 (m, 1H), 1.40–1.24 (m, 32H), 0.93–0.89 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 140.9, 125.5, 122.8, 120.2, 118.6, 108.9, 47.7, 37.9, 31.9, 31.8, 29.9, 29.6, 29.5, 29.3, 29.2, 26.6, 22.7, 22.6, 14.1.

1,2-Bis(9'-(2"-octyldodecyl)carbazol-3'-yl)ethane-1,2-dione (8). Aluminum chloride (0.67 g, 5 mmol) and 3 mL of anhydrous 1,2-dichloroethane were placed into a 100-mL three-necked flask equipped with magnetic stirrer, thermometer, and dropping funnel. The resultant suspension was cooled to –20°C, and a solution of 0.1 mL (0.142 g, 1.12 mmol) of oxalyl chloride in 0.5 mL of anhydrous 1,2-dichloroethane was added; the mixture was stirred for 5 min, and a solution of 1 g (2.23 mmol) of 9-(2'-octyldodecyl)-9H-carbazole (**7**) in 0.18 mL (0.17 g, 2.2 mmol) of dry pyridine and 0.5 mL of anhydrous 1,2-dichloroethane was added dropwise. The reaction mixture was stirred for 20 min at –20°C, allowed to warm to 0°C, poured into 100 g of crushed ice, and extracted with dichloromethane (3 × 50 mL). The organic extract was washed with water until neutral pH, dried with $MgSO_4$, and concentrated in a vacuum. The residue was purified by column chromatography with gradient elution (PE, then PE : EtOAc = 3 : 1) to give 0.38 g of viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.81 (s, 2H), 8.22 (d, J = 8.5 Hz, 2H), 8.11 (d, J = 7.7 Hz, 2H), 7.47 (dt, J = 17.9, 8.1 Hz, 6H), 7.29 (t, J = 7.5 Hz, 2H), 4.19 (d, J = 7.3 Hz, 4H), 2.12 (s, 2H), 1.43–1.16 (m, 64H), 0.91–0.83 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 195.2, 144.7, 141.8, 12.9, 126.8, 125.0, 124.2, 123.2, 123.2, 121.0, 120.5, 109.8, 109.3, 48.06, 37.96, 31.90, 31.83, 30.01, 30.0, 29.7, 29.7, 29.7, 29.6, 29.4, 29.3, 26.7, 22.8, 22.8, 14.3, 14.2.

For $C_{66}H_{96}N_2O_2$ anal. calcd. (%): C, 83.49; H, 10.19; N, 2.95.

Found (%): C, 83.23; H, 10.09; N, 2.81.

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