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Novel [2.2]Paracyclophane−Fluorene-Based Conjugated Copolymers: Synthesis, Optical, and Electrochemical Properties

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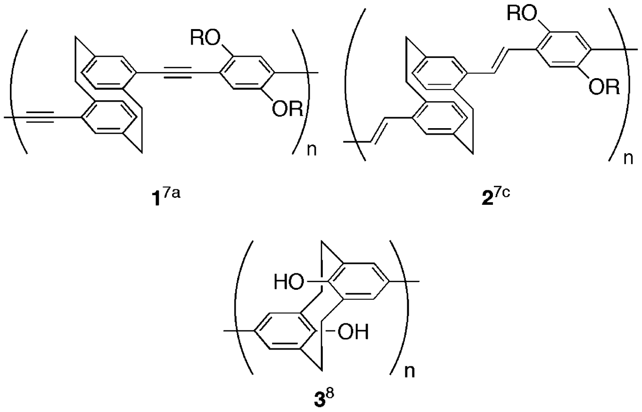
ABSTRACT: Novel through-space π-conjugated polymers having [2.2]paracyclophane and fluorene units were synthesized by the Heck coupling reaction. The polymers **6a**−**c** possess good solubility in common organic solvents and good thermal stability. All of the polymers **6a**−**c** exhibited bright blue emission with high photoluminescence (PL) efficiencies of 67−72% in solution. The HOMO and LUMO energy levels of the polymer **6a** were estimated from the cyclic voltammogram. The first organic electroluminescence (EL) material using a cyclophane-containing polymer was successfully fabricated and showed a bluish-green light at around 500 nm.

Introduction

[2.2]Paracyclophane, which has two layered benzene rings, has attracted much attention with regard to its structure, reactivity, and physical properties.[1] A number of paracyclophane derivatives have been prepared, and their unique properties, especially structural and electronic properties due to characteristic interactions between the two cofacial π-electron systems, have been investigated in detail.[2] In addition, several polymers having a [2.2]paracyclophane skeleton in the main chain[3] or in the side chain[4] have been prepared thus far. However, as to studies of cyclophane-containing π-conjugated polymers, there have been only a few reports,[5,6] and the structures and properties of these polymers have not been studied due to their poor solubility in common organic solvents. Recently, we reported the first preparation and physical properties of well-defined π-conjugated polymers (Chart 1)[7] having cyclophane derivatives as the key unit, in which the obtained polymers showed an extension of π-delocalization via the through-space with $\pi-\pi$ stacking according to the UV−vis absorption spectra and exhibited an intense luminescence in solution.

On the other hand, charge transfer is essential to the expression of conductivity and electroluminescence (EL), in which charge-hopping between the π-aromatic systems plays an important role. From this standpoint, Mizogami and Yoshimura have reported the first synthesis of polymetacyclophane (Chart 1) by polycondensation reaction of an oxidative dimer of 8,16-dihydroxy-[2.2]metacyclophane, and this polymer exhibited a conductivity of 0.25 S cm^{-1} by doping with H_2SO_4 vapor.[8] Incorporation of [2.2]paracyclophane bearing π-stacked benzene rings into the conjugated polymer backbone is expected for not only efficient charge-hopping but also effective enhancement of the aromatic content of the obtained materials. Therefore, [2.2]-paracyclophane-containing conjugated polymers are promising candidates for high-performance EL devices.

Chart 1



1[7a] **2**[7c] **3**[8]

Fluorene derivatives have a rigid planar structure, and their physical properties and solubility can easily be tuned by substitution at the C9 position. These are important building blocks in constructing the blue-emitting polymers due to their high efficiency and good thermal as well as air stability. In the present study, we prepared novel π-conjugated polymers based on poly(*p*-phenylenevinylene) (PPV) derivatives having [2.2]-paracyclophane and fluorene units alternatively in the main chain, and the optical and electrochemical behaviors of the titled polymers were investigated.

Results and Discussion

As shown in Scheme 1, monomers **4** and **5a**−**c** were easily polymerized to the corresponding polymers **6a**−**c** with $Pd(OAc)_2/P(o\text{-tolyl})_3/Bu^n{}_3N$ in DMF at 100 °C for 72 h according to the standard Heck coupling reaction method.[9] After the reaction was completed, inorganic byproducts were filtered off, and the filtrate was reprecipitated into a large amount of MeOH to obtain the crude polymers **6a**−**c**. The polymers **6a**−**c** were dissolved in toluene and washed three times with NH_3(aq) to remove the palladium species. Finally, purification for improvement of EL device performance using the recyclable preparative HPLC was carried out to give the corresponding polymers **6a**−**c** in good yields of 86−98% as a light yellow powder. The results are summarized in Table 1. Previously, we synthesized polymer **2** (Chart 1) under the modified Heck reaction condition, i.e., the $PdCl_2(PPh_3)_2/Bu^n{}_4NI/K_2CO_3$ system,[7c,10] to over-

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Scheme 1

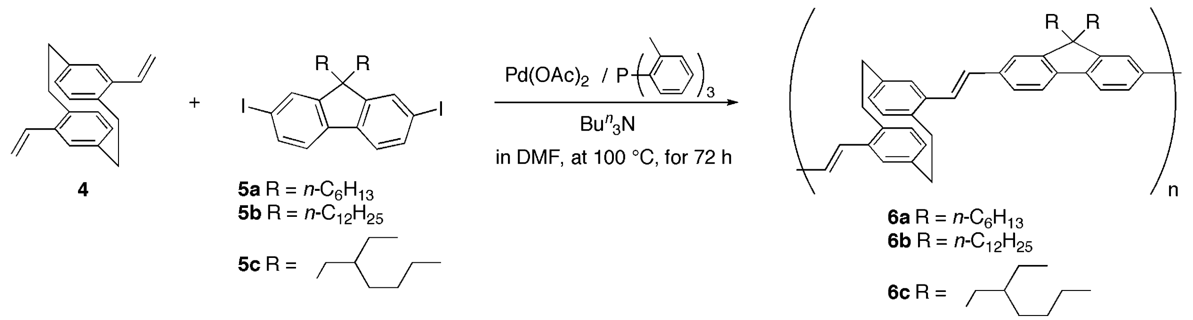

Table 1. Syntheses of the Polymers 6a−c[a]

polymer	R	yield[b]/%	M_w[c]	M_n[c]	M_w/M_n[c]
6a	*n*-hexyl (**5a**)	96	10 000	5200	1.9
6b	*n*-dodecyl (**5b**)	98	12 000	5800	2.1
6c	2-ethylhexyl (**5c**)	86	13 600	6400	2.1

[a] Polymerization was carried out at 100 °C for 72 h under N_2. [b] Isolated yields. [c] GPC ($CHCl_3$), polystyrene standards.

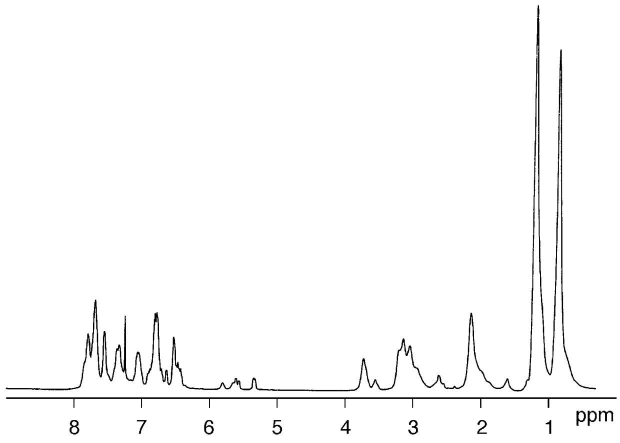

Figure 1. ^1H NMR spectrum of **6a** in $CDCl_3$.

come the steric repulsion between the palladium catalyst and the alkoxy group attached to the benzene ring. In the present reaction, it is assumed that the oxidative addition of 2,7-diiodo-9,9-dialkylfluorenes **5a**−**c** to the palladium center occurs more smoothly due to less steric hindrance. All polymers had good solubility in common organic solvents such as THF, $CHCl_3$, CH_2Cl_2, and toluene. In addition, the polymers could be processed into a self-standing thin film by casting or spin-coating from toluene solution and were found to be air stable in solution and in the solid state.

The molecular weight measurements were performed by gel permeation chromatography (GPC) in eluent $CHCl_3$ using the calibration curve of polystyrene standards, as listed in Table 1. For example, the number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the molecular weight distribution (M_w/M_n) of the polymer **6a** obtained by run 1 were $M_n = 5200$, $M_w = 10\ 000$, and $M_w/M_n = 1.9$, which resulted in estimation of the number-average degree of polymerization as 9.

These polymers were characterized by their ^1H and ^{13}C NMR spectra. In the ^1H NMR spectrum of **6a** in $CDCl_3$ (Figure 1), the signals of the alkoxy side chains dominated in the region of 0.80−2.2 ppm, and the bridged methylenes of the paracyclophane unit appeared at 2.8−3.8 ppm. The signals of the aromatic and olefinic protons were between 6.5 and 7.8 ppm. The ^1H NMR spectrum of **6a** also showed peaks at 5.3−5.8 ppm attributed to the terminal vinyl protons. The integral ratio of the terminal vinyl protons with the alkyl side chain of the fluorene unit in the polymer chain resulted in estimation of the number-average degree of polymerization as 10 ($M_n = 6169$). This calculated value is in good agreement with that from GPC ($n = 9$ and $M_n = 5200$).

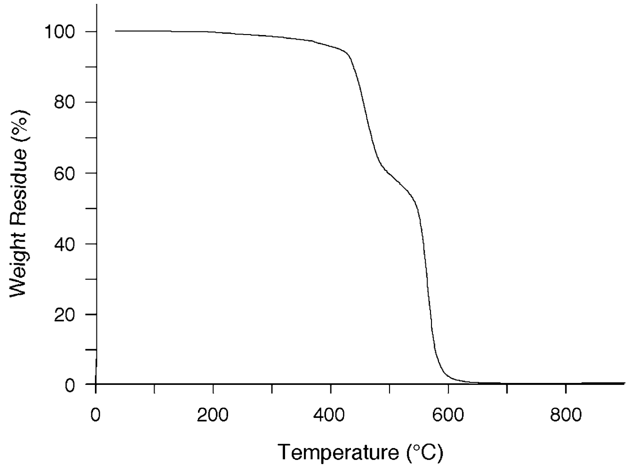

Figure 2. Thermogravimetric analysis (TGA) of **6a** under air (10 °C/min).

The thermal stability of the polymer **6a** was evaluated by thermogravimetric analysis (TGA) under air, and the result is shown in Figure 2. This polymer possessed good thermal stability with a 10% weight loss temperature at 433 °C, at a heating rate of 10 °C/min. The decomposition of **6a** involved two steps. The first step started from 415 °C, which may be assigned to thermal decomposition of the alkyl side chain of the polymer, and the second one, which started from around 520 °C and completed at 630 °C, is attributed to the decomposition of the polymer backbone.

The optical properties of the polymers **6a**−**c** are summarized in Table 2. The absorption spectrum of **6a** solution as a representative polymer is shown in Figure 3. The polymer **6a** shows a strong absorption peak at 372 nm in $CHCl_3$ at room temperature (run 1), which is the $\pi-\pi^*$ transition band of the PPV polymer backbone. In addition, the absorption spectrum of the thin film of **6a** showed a peak maximum at 373 nm. This value is almost same as that obtained in solution. On the basis of the absorption edge in the film state (around 450 nm), the band gap energy of **6a** is approximately 2.74 eV. In the fluorescence emission spectra of the polymers **6a**−**c** in dilute $CHCl_3$ solution at room temperature on excitation at 375 nm, the emission peaks

Table 2. Optical Properties of the Polymers 6a−c

	UV $\lambda_{max}{}^{a}$/nm		PL $\lambda_{max}{}^{a,b}$/nm		
polymer	solution	film	solution	film	$\Phi_{PL}{}^{c}$
6a	372	376	426	484	0.70
6b	376	380	426	481	0.67
6c	377	378	426	485	0.72

[a] Absorption and emission spectra were recorded in dilute $CHCl_3$ solutions at room tsemperature. [b] Excited at 375 nm (1.0×10^{-5} M). [c] PL efficiencies in $CHCl_3$ determined relative to 9-anthracenecarboxylic acid in CH_2Cl_2.

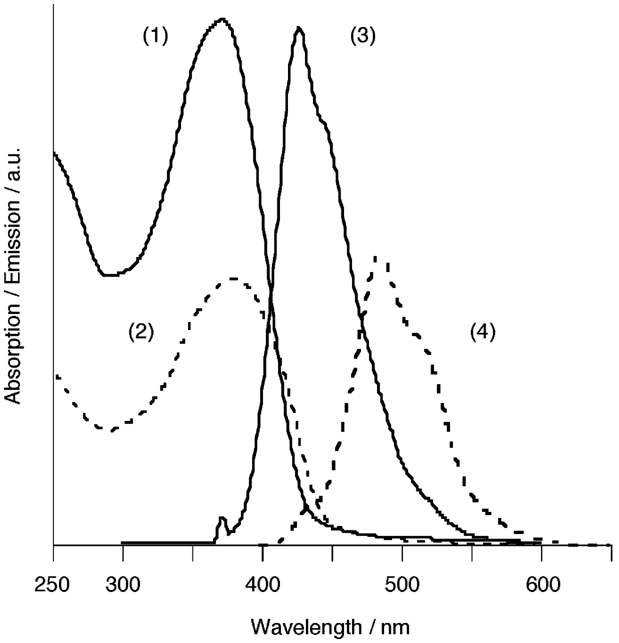

Figure 3. UV−vis spectra of **6a** (1) in $CHCl_3$ and (2) in the film state and fluorescence emission spectra of **6a** (3) in $CHCl_3$ and (4) in the film state on excitation at 375 nm.

were observed at 426 nm in the visible blue region (Table 2 and Figure 3). The polymer solutions showed a high quantum efficiency; for example, **6a** had an efficiency of 0.70 in $CHCl_3$ solution at room temperature, as demonstrated by using 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard ($\Phi = 0.442$).[11] In the solid thin film of **6a**, the emission peak maximum at 485 nm was red-shifted approximately 60 nm from that in solution (Table 2 and Figure 3). This result indicates a relatively strong intermolecular interaction in the solid state. The shapes and peaks of the absorption spectra and emission spectra of **6a**−**c** were independent of the nature of the alkyl side chains both in solution and in the solid state.

The cyclic voltammetry of the polymer **6a** film coated on ITO glass electrode in CH_3CN solution of 0.1 M Bu_4NClO_4 was performed in a three-electrode cell using a Pt counter electrode and a Ag/AgCl reference electrode. As shown in the cyclic voltammogram (Figure 4), the oxidation process gave the onset peak at about 0.85 V vs Ag/Ag^+. In the cathodic scan, the onset reduction potential was observed at about −1.92 V. Accordingly, both the HOMO and LUMO energy levels of **6a** can be calculated by comparison with the onset oxidation potential of ferrocene below vacuum,[12] and the values are −5.5 and −2.8 eV, respectively. The band gap is estimated to be about 2.7 eV, which is in close agreement with the calculated value of the optical band gap obtained from UV−vis spectrum of **6a** in the film state.

The electroluminescent (EL) properties of the polymer **6a** were also examined. Single-layer (ITO/**6a**/Al) and

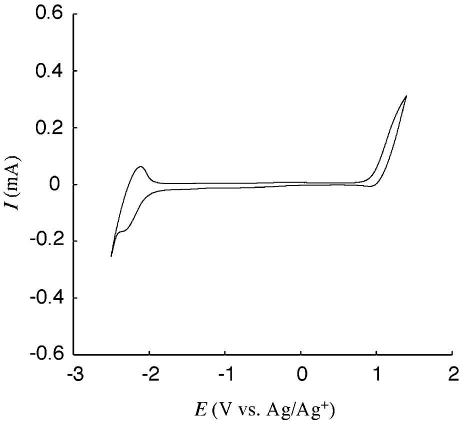

Figure 4. Cyclic voltammogram of the polymer **6a** film coated on the ITO plate electrode in CH_3CN containing 0.1 M Bu_4NClO_4 as a supporting electrolyte (vs Ag/Ag^+) at a scan rate of 100 mV/s.

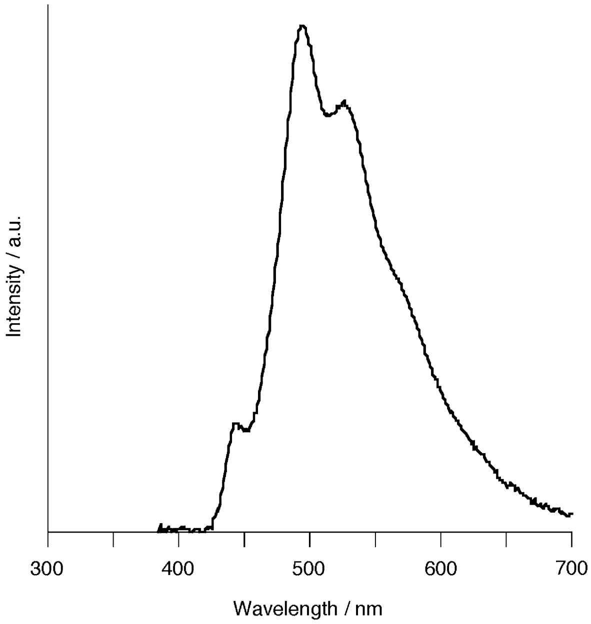

Figure 5. Electroluminescence (EL) spectrum of the device ITO/PEDOT-PSS/**6a**/BCP/Alq/LiF/Al.

two-layer (ITO/PEDOT-PSS/**6a**/Al) devices, where a polymer blend including a conducting polymer PEDOT, poly(3,4-ethylene dioxythiophene), and PSS, poly(4-styrenesulfonic acid), was used as a hole-transport layer, did not show high performance with weak emissions. To improve the device performance, BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) was used as a hole-blocking layer on **6a**, and a multilayered device with a configuration of ITO/PEDOT-PSS/**6a**/BCP/Alq/LiF/Al was fabricated. A typical EL spectrum from this device is shown in Figure 5. The EL spectrum showed a maximum peak at 490 nm and a shoulder peak around 510 nm, which is very similar to the PL spectrum of the corresponding polymer film. The current density−voltage−brightness curve is drawn in Figure 6. The device exhibited a bluish-green light with a turn-on voltage at 13 V when the thickness of the emissive polymer layer was approximately 110 nm. The luminescence brightness reached 150 cd/m^2 at a drive voltage of 19 V and a current density of 546 A/m^2. The external quantum efficiency of this device from the polymer **6a** was found to be 0.88% at 38 cd/m^2 with a bias of 14 V. The onset potential, brightness, and quantum efficiency

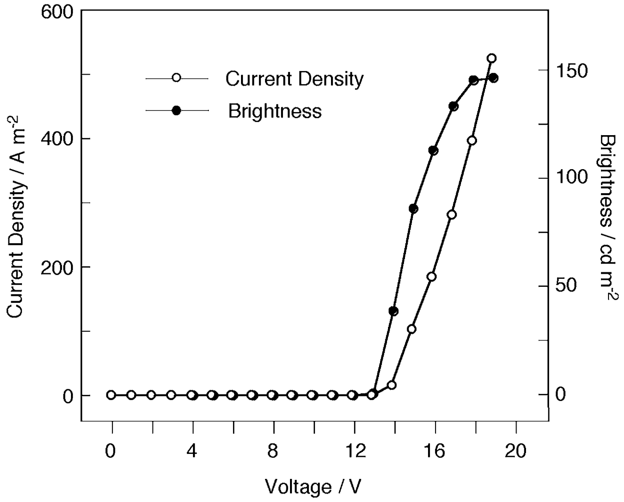

Figure 6. Current−voltage−brightness characteristics of the device ITO/PEDOT-PSS/**6a**/BCP/Alq/LiF/Al.

are expected to be enhanced by optimization, e.g., the thickness of the emissive layer, the combination of each charge-transporting layer, and alkyl substituent at the C9 position of the fluorene unit in the polymer backbone.

Conclusions

Novel π-conjugated polymers with [2.2]paracyclophane and fluorene appended to the PPV backbone were prepared by the Heck coupling reaction. These polymers were soluble in common organic solvents, and self-standing thin films of the polymers were obtained easily by casting or spin-coating from a toluene solution. These polymers possessed good thermal stability. The polymers exhibited strong blue photoluminescence in solution and bluish-green photoluminescence in the solid state. According to the cyclic voltammogram of the polymer **6a**, the HOMO and LUMO energy levels were estimated to be −5.5 and −2.8 eV, respectively. The light-emitting diode of the polymer also emitted bluish-green light with a maximum peak around 490 nm and a shoulder peak around 510 nm.

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 instrument at 270 and 67.5 MHz, respectively. All samples were analyzed in $CDCl_3$, and the chemical shift values were expressed relative to Me_4Si as an internal standard. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. UV−vis spectra were obtained on a JASCO V-530 spectrophotometer, and samples were analyzed in $CHCl_3$ at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in $CHCl_3$ at room temperature. Gel permeation chromatography was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using $CHCl_3$ as an eluent after calibration with standard polystyrene. Thermogravimetric analysis (TGA) was made on a Seiko EXSTAR 6000 instrument (10 °C/min). Cyclic voltammetry was carried out under a nitrogen atmosphere using a BAS CV-50W voltammetric analyzer with a 0.10 M CH_3CN solution containing Bu_4NClO_4 as an electrolyte at a scan rate of 100 mV/s. Polymer films were prepared on the glass coated with indium−tin oxide (ITO) by spin-coating from the corresponding toluene solutions and dried under vacuum. A platinum wire counter electrode and a Ag/AgCl reference electrode were used. EL device fabrication and measurements were performed at Konica Minolta Technology Center, Inc. Further purification of the obtained polymers for EL device fabrication was carried out on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., model 918R) equipped with JAIGEL-1H and 2H columns (GPC) using $CHCl_3$ as an eluent.

Materials. *N*,*N*-Dimethylformamide (DMF) was distilled from calcium hydride. $Bu^{n}_{3}N$ was distilled from KOH. Tri-*o*-tolylphosphine (P(*o*-tolyl)$_3$) and $Pd(OAc)_2$ were obtained commercially and used without further purification. 4,16-Divinyl-[2.2]paracyclophane (**4**) was prepared as described in the literature with minor modification.[2a,7c] 2,7-Diiodo-9,9-dialkylbenzenes **5a**−**c** were prepared as described in the literature.[13] All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques.

Polymerization. A typical procedure is as follows. A 50 mL Pyrex flask was charged with **4** (52 mg, 0.20 mmol), **5a** (117 mg, 0.20 mmol), $Pd(OAc)_2$ (4.6 mg, 0.020 mmol), P(*o*-tolyl)$_3$ (30 mg, 0.10 mmol), $Bu^{n}_{3}N$ (0.30 mL), DMF (2.0 mL), and a stirring bar under a flow of nitrogen. The reaction was carried out at 100 °C for 72 h with stirring. The resulting solution was concentrated and poured into a large amount of MeOH to give the crude polymer as a yellowish-green powder. This crude polymer was dissolved into toluene and washed three times with NH_3(aq). The organic layer was dried over $MgSO_4$. After filtration of $MgSO_4$, the solvent was evaporated and dried in vacuo. The resulting yellow residue was dissolved in $CHCl_3$ and was purified by a recycling preparative HPLC using $CHCl_3$ as an eluent. Finally, the solvent was concentrated and poured into a large amount of MeOH to give the yellow polymer. The obtained polymer was washed with MeOH several times. After the product was dried under reduced pressure, a bright yellow polymer **6a** was obtained.

6a. Yield: 113 mg, 0.19 mmol, 96%. ^{1}H NMR (270 MHz, $CDCl_3$); δ 0.79 (br, 10H), 1.13 (m, 12H), 2.09 (br, 4H), 2.89−3.09 (m, 6H), 3.73 (br, 2H), 6.54 (m, 2H), 6.79 (m, 4H), 7.08 (m, 4H), 7.34−7.80 (m, 6H). ^{13}C NMR (67.5 MHz, $CDCl_3$); δ 14.0, 22.1, 23.8, 29.9, 31.4, 33.4, 34.6, 40.7, 55.2, 119.9, 121.5, 125.2, 126.3, 130.1, 133.7, 136.8, 137.4, 137.6, 138.1, 139.4, 140.0, 140.8, 151.7.

6b. Yield: 151 mg, 0.19 mmol, 98%. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 0.69 (br, 4H), 0.85 (br, 6H), 1.18 (m, 36H), 2.07 (br, 4H), 2.88−3.10 (m, 6H), 3.63 (br, 2H), 6.48 (m, 2H), 6.71 (m, 4H), 7.04 (m, 4H), 7.21−7.72 (m, 6H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 141, 22.7, 23.9, 29.3, 29.6 (overlapping signals), 31.9, 33.4, 34.6, 40.4, 55.0, 119.9, 121.3, 125.5, 126.1, 130.0, 132.9, 133.0, 133.7, 135.3, 136.8, 137.7, 139.5, 140.5, 151.7.

6c. Yield: 112 mg, 0.17 mmol, 86%. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 0.42−1.10 (m, 30H), 2.12 (br, 4H), 3.00 (m, 6H), 3.66 (m, 2H), 6.48 (m, 2H), 6.72 (m, 4H), 7.01 (m, 4H), 7.26 (m, 2H), 7.60 (m, 4H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 10.4, 14.0, 22.7, 27.1, 28.3, 33.0, 33.5, 34.0, 34.5, 44.4, 54.9, 114.3, 119.8, 125.8, 126.1, 130.1, 132.9, 133.6, 135.3, 136.3, 137.5, 137.7, 139.3, 140.8, 151.2.

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(11) The absorbance of each sample was below 0.05 at the excitation wavelength at 375 nm, in the measurement of the fluorescence quantum yield. The quantum yield (Φ_{unk}) of unknown sample was calculated by the following equation: $\Phi_{\mathrm{unk}} = \Phi_{\mathrm{std}}[A_{\mathrm{std}}F_{\mathrm{unk}}/A_{\mathrm{unk}}F_{\mathrm{std}}][n_{\mathrm{D,unk}}/n_{\mathrm{D,std}}]^2$, where A_{std} and A_{unk} are the absorbance of the standard and unknown sample, respectively, F_{std} and F_{unk} are the corresponding relative integrated fluorescence intensities, and n_{D} is the refractive index [CH_2Cl_2 ($n_{\mathrm{D}} = 1.424$) and $CHCl_3$ ($n_{\mathrm{D}} = 1.446$) were used].

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