Molecular Engineering of Organic Sensitizers Containing *p*-Phenylene Vinylene Unit for Dye-Sensitized Solar Cells

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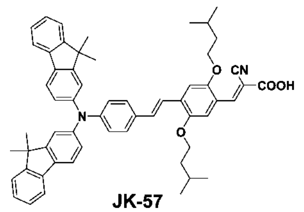
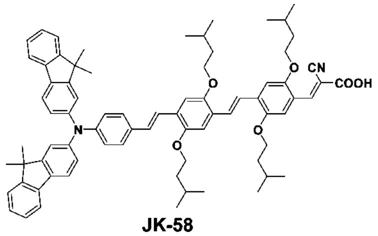


JK-57



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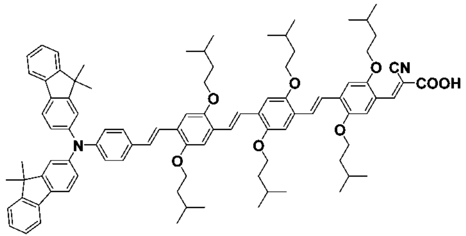

JK-59

Three organic sensitizers containing bis-dimethylfluorenyl amino donor and a cyanoacrylic acid acceptor bridged by *p*-phenylene vinylene unit were synthesized. The power conversion efficiency was quite sensitive to the length of bridged phenylene vinylene groups. A nanocrystalline TiO_2 dye-sensitized solar cell was fabricated using three sensitizers. The maximum power conversion efficiency of **JK-59** reached 7.02%.

Introduction

Global warming and depletion of fossil fuels have led to a greater focus on renewable energy sources in recent years. In this respect, dye-sensitized solar cells are attracting widespread interest for a new renewable energy source because of the low cost and high efficiency.[1] Several Ru(II) polypyridyl complexes have achieved power conversion efficiencies above 10% under standard soar illumination (global air mass 1.5).[2] Although the ruthenium-based sensitizers exhibited high efficiency and good stability, they are quite expensive and hard to purify compared to the organic sensitizers. Some organic dyes show the impressive photovoltaic performance having efficiencies in the range of 7−9%.[3] One of the main drawbacks of organic sensitizers is the shape and narrow absorption band in the blue region. The optimal organic sensitizer for solar cell applications should be broadened and red-shifted. All of the organic dyes have a structure with donor-to-acceptor moieties bridged by a π-con-

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jugation unit. In most organic sensitizers, the amine derivatives act as the electron donor while a 2-cyanoacrylic acid or rhodanine moiety acts as the electron acceptor. These two parts are connected by π-conjugation systems such as the methine unit or thiophene chain. Recently, a successful approach was introduced by incorporating a π-conjugation system such as the thiophene chain into the organic framework, [4] which not only increases the molar extinction coefficient of the organic sensitizer but also increases the stability. Moreover, the introduction of thiophene chain led to the broadening of the absorption spectra and gave a red shift in the absorption spectrum. As part of our efforts to investigate the structural modifications of π-conjugated unit that can enhance the efficiency and stability, phenylene vinylene units instead of thiophene chain have been synthesized. The π-conjugated oligomers are intensively studied for use in optoelectronic devices because their chemical structure facilitates tuning of electronic properties. In particular, oligo(*p*-phenylene vinylene)s are being actively investigated for use in solar cells and light-emitting diodes due to their stability and high luminescent efficiency. [5] In this paper, we report three new organic sensitizers (**JK-57**, **JK-58**, and **JK-59**) containing bis-dimethylfluorenyl amino group as electron donor and cyanoacrylic acid as electron acceptor bridged by phenylene vinylene unit. We also describe the effect of bridged structural modifications on the photovoltaic properties, electric, and optical properties.

Results and Discussion

Scheme 1 illustrates the stepwise synthetic protocol of organic dyes **JK-57**, **JK-58**, and **JK-59**. A Williamson etherification of methylhydroquinone with 1-bromo-3-methy-lbutane gave 1,4-bis(isopentoxy)-2-methylbenezene **1**.[6] Compound **3** was obtained by bromination reaction of **1** using *N*-bromosuccinimide (NBS) and 2,2′-azobis(2-methylpropionitrile) (AIBN) followed by a Michaelis−Arbuzor reaction.[7] Formylation of **3** was carried out using α,α-dichloromethyl methyl ether and titanium(IV) chloride.[8] The formyl group of diethyl(4-formyl-2,5-bis(isopentoxy)phenyl)methyl phosphonate **4** was protected with neopentyl glycol to afford acetal **5**. Carbaldehyde **7** was prepared from **6** by means of a Vilsmeier−Haack reaction.[9] Coupling reaction of carbaldehyde **7** with diethyl(2,5-bis(isopentoxy)-4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)methylphosphonate **5** under Horner−Emmons−Wittig reaction[10] led to intermediate **8**. The phenylene vinylene derivative **8** was converted into its corresponding aldehyde **9** by dedioxanylation with trifluoroacetic acid (TFA). The aldehyde **9**, upon reaction with cyanoacetic acid in the presence of piperidine in acetonitrile, produced the **JK-57** dye. The two sensitizers **JK-58** and **JK-59** were readily synthesized by the stepwise addition of the aldehyde **9** with **5** and **12** with **5**, respectively.

Figure 1 shows the absorption and emission spectra of the **JK-57**, **JK-58**, and **JK-59** sensitizers in THF, and the data are collected in Table 1. The absorption spectrum of **JK-57** exhibited two absorption bands at 457 and 369 nm, which are due to the $\pi-\pi^*$ transitions of the conjugated system. Under the same conditions, the **JK-58** sensitizer displays absorption bands at 466 and 373 nm. The red-shifted band about 10 nm of **JK-58** compared to that of **JK-57** is due to the increase of the π-conjugation systems by phenylene vinylene. A progressive red-shifted band of **JK-59** compared to **JK-58** is due to the introduction of one more phenylene vinylene group to **JK-58**. The absorption spectra of **JK-57**−**JK-59** on TiO_2 film are broadened and red-shifted due to the interaction of the anchoring group with the surface titianium ions (Figure 2). Such a broadening and red-shift have been reported in several organic sensitizers on TiO_2 electrodes.[11] The threshold wavelength of absorption spectra for sensitizers **JK-57**, **JK-58**, and **JK-59** are 560, 600, and 620 nm, respectively, indicating that the stepwise introduction of a phenylene vinylene into the organic framework expanded the conjugation resulting in a wide absorption in the visible region. The wide absorption and red shift of absorption maximum in the visible region is desirable for light harvesting of solar energy. We observed that the organic dyes **JK-57**−**JK-59** exhibited strong luminescence maxima of 575−612 nm when they are excited within their $\pi-\pi^*$ bands at 298 K.

To thermodynamically evaluate the possibility of electron transfer from the excited-state of the dye to the conduction band of TiO_2 electrode, electrochemical properties of the **JK-57**, **JK-58**, and **JK-59** sensitizers were scrutinized by cyclic voltammetry in THF solvent containing 0.1 M tetrabutylammonium hexafluorophosphate (Figure 6 in Supporting Information). The oxidation potential of **JK-57** exhibited a quasi-reversible behavior at 1.13 V (versus NHE) with a peak separation of 0.12 V, which is attributed to the oxidation of 3-(5-(*N*,*N*-bis(9,9-dimethylfluoren-2-yl)aminophenyl)group. Under similar conditions, dyes **JK-58** and **JK-59** show a quasi-reversible couple at 1.13 and 1.09 V, respectively. Analysis of the quasi-reversible process in three dyes shows that the oxidation potentials are close, due to the similar donor groups. The reduction potentials of **JK-57**−**JK-59** calculated from the oxidation potential and

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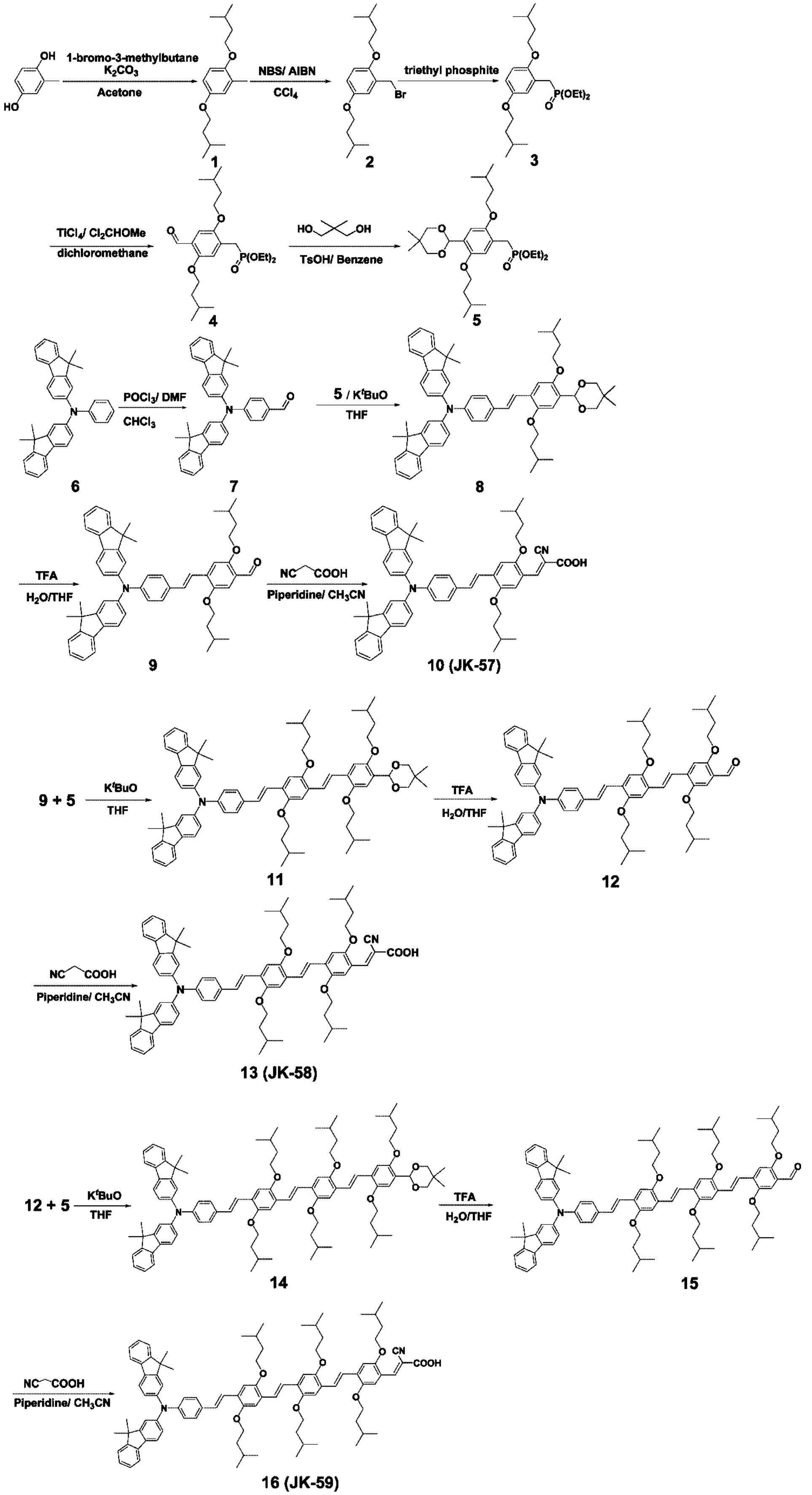
SCHEME 1. Schematic Diagram for the Synthesis of Organic Sensitizers JK-57, JK-58, and JK-59



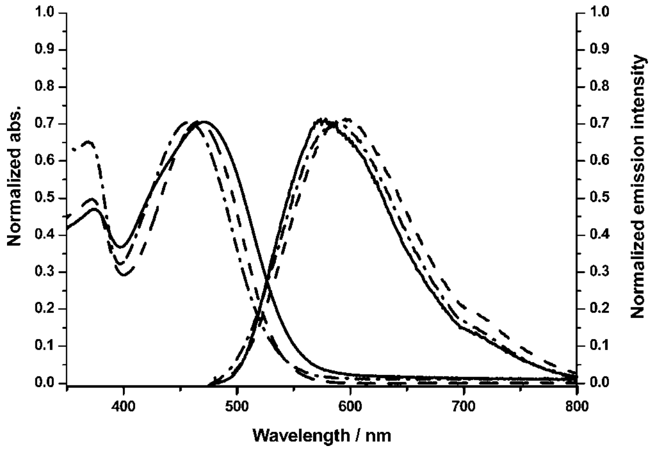


FIGURE 1. Absorption and emission spectra of **JK-57** (dash dot line), **JK-58** (dash line), and **JK-59** (solid line) in THF.

the E_{0-0} determined from the intersection of absorption and emission spectra are listed in Table 1.[22] The excited-state oxidation potential (E^*_{OX}) of the sensitizers (**JK-57**, −1.28 V; **JK-58**, −1.25 V; **JK-59**, −1.27 V versus NHE) is much negative than the conduction band level of TiO_2 at approximately −0.5 V versus NHE, ensuring that there is enough driving force for the electron injection into the conduction band of TiO_2.

In order to determine the photophysical properties, molecular orbital calculations of **JK-57**−**JK-59** sensitizers were performed with the TD-DFT on B3LYP/3-21G* (Figure 3). The calculation illustrates that the HOMO of **JK-57** is delocalized over the π-conjugated system centered on the amino phenyl unit, and LUMO is delocalized over the cyanoacrylic unit through the phenylene vinylene group. From these results, we could induce that the photoinduced electron transfer from **JK-57**, **JK-58**, and **JK-59** dyes to TiO_2 electrode can efficiently occur by the HOMO → LUMO transition.

Figure 4 shows the incident monochromatic photon-to-current conversion efficiency (IPCE) for the DSSCs based on the three dyes. The IPCE data of **JK-57** sensitizer plotted as a function of excitation wavelength exhibits a high plateau at 68%. The decline of the IPCE above 570 nm toward the red is caused by the decrease in the extinction coefficient of **JK-57**. The **JK-58** and **JK-59** sensitizers' IPCE spectra are broadened and red-shifted by about 40 nm compared to **JK-57** as a result of extended π-conjugation, which is consistent with the absorption spectra of the **JK-58** and **JK-59** sensitizers. The onset of the IPCE spectra of the **JK-58** and **JK-59** sensitized cells are 701 and 720 nm. Figure 4 also shows the photocurrent−voltage (J−V) curves of three DSSCs fabricated with TiO_2 films, which are anchored with **JK-57**−**JK-59**. The photovoltaic performance of the device is listed in Table 1. Under standard global AM 1.5 solar condition, the **JK-57**-sensitized cell gave a short circuit photocurrent density (J_{sc}) of 10.50 mA cm^{-2}, open circuit voltage (V_{oc}) of 0.69 V, and a fill factor of 0.73, corresponding to an overall conversion efficiency η of 5.34%. Under the same conditions, an overall conversion efficiency (η) of 6.89% for **JK-58** and 7.02% for **JK-59** sensitized cells (for **JK-58**: short-circuit photocurrent density, $J_{\mathrm{sc}} = 13.26$ mA cm^{-2}; open-circuit photovoltage, $V_{\mathrm{oc}} = 0.70$ V; fill factor, ff = 0.71. For **JK-59**: $J_{\mathrm{sc}} = 14.26$ mA cm^{-2}; $V_{\mathrm{oc}} = 0.70$ V; ff = 0.70) was obtained. The J_{sc} enhancement of **JK-58** and **JK-59** relative to **JK-57** can be related to the expansion of the π-conjugated system of the dyes.

Figure 5 shows the electron-diffusion coefficient (D_{e}) and lifetime (τ_{e}) of the DSSCs employing different dyes (i.e., **N719**, **JK-57**, **JK-58**, and **JK-59**) as a function of the J_{sc}. The D_{e} and τ_{e} values were determined by the photocurrent and photovoltage transients induced by a stepwise change in the laser light intensity controlled with a function generator.[12] The D_{e} value was obtained by a time constant (τ_{c}) determined by fitting a decay of the photocurrent transient with $\exp(-t/\tau_{\mathrm{c}})$ and the TiO_2 film thickness (ω) using the equation $D_{\mathrm{e}} = \omega^2/(2.77\tau_{\mathrm{c}})$. The τ value was also determined by fitting a decay of photovoltage transient with $\exp(-t/\tau)$. The J_{sc} values in the x-axis increased with an increase in the initial laser intensity controlled by ND filters with different optical densities. The D_{e} values of the photoanodes adsorbing the organic dyes are shown to be very similar to those of **N719** at the identical short-circuit current conditions. Meanwhile, the significant difference in the τ_{e} values was observed among the cells employing different dyes. The different τ_{e} values might be caused by the different molecular size and structures of the dyes.[13] In particular, the τ_{e} values of **JK-59** were smaller than those of **JK-58**, demonstrating the decreased amount of dyes on TiO_2 due to the steric hinderence caused by the bulky structure. We have measured the amounts of dyes adsorbed on a 10 μm TiO_2 film. The adsorbed amounts of 2.27×10^{-7} mol/cm^2 for **JK-57**, 7.81×10^{-8} mol/cm^2 for **JK-58**, and 3.45×10^{-8} mol/cm^2 for **JK-59** are observed. It seems that the electron recombination rates were dependent upon the molecular structures and the intermolecular $\pi-\pi$ stacking interactions of the dyes due to the different coverages on the TiO_2 surface. The results of the electron lifetime are well consistent with those of the V_{oc} shown in Table 1. The conflicting contribution of diffusion coefficient and lifetime can be combined and expressed by means of the diffusion length (L_{d}). Diffusion length of electrons is denoted as $L_{\mathrm{d}} = (D_{\mathrm{e}} \cdot \tau_{\mathrm{e}})^{0.5}$.[14] The diffusion length was shown to increase in the order of **N719** (17.02 μm) > **JK-58** (15.29 μm) > **JK-59** (14.27 μm) > **JK-57** (12.76 μm).

In summary, we have designed and synthesized three organic sensitizers containing amorphous *N*,*N*-bis(9,9-dimethylfluoren-2-yl)aniline unit bridged by phenylene vinylene units. The power conversion efficiency of the DSSCs based on the three sensitizers was shown to be sensitive to the conjugation length of bridged phenylene vinylene groups. The maximum power conversion efficiency of the DSSCs using the **JK-59** sensitizer reaches 7.02%.

Experimental Section

Preparation of DSSC. For the preparation of DSSC, fluorine-doped tin oxide (FTO) glass plates (2.3 mm thickness) were cleaned

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TABLE 1. Optical, Redox, and DSSC Performance Parameters of Dyes

dye	$\lambda_{abs}{}^{a}$/nm(ϵ/M^{-1}cm^{-1})	$E_{ox}{}^{b}$ (V)	$E_{0-0}{}^{c}$ (V)	$E_{LUMO}{}^{d}$ (V)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η^{e} (%)
JK-57	369 (35710), 457 (38650)	1.13	2.41	−1.28	10.50	0.69	0.73	5.34
JK-58	373 (49670), 466 (70056)	1.13	2.38	−1.25	13.26	0.73	0.71	6.89
JK-59	375 (45590), 472 (68390)	1.09	2.38	−1.27	14.26	0.70	0.70	7.02
N719	535 (14700)				17.33	0.73	0.72	9.02

[a] Absorption spectra were measured in THF solution. [b] Oxidation potentials of dyes on TiO_2 were measured in THF with 0.1 M $(n\text{-}C_4H_9)_4NPF_6$ with a scan rate of 50 mVs^{-1} (vs NHE). [c] E_{0-0} was determined from intersection of absorption and emission spectra in THF. [d] E_{LUMO} was calculated by $E_{ox} - E_{0-0}$. [e] Performances of DSSCs were measured with 0.18 cm^2 working area. Key: ϵ, absorption coefficient; E_{ox}, oxidation potential; E_{0-0}, voltage of intersection point between absorption and emission spectra; J_{sc}, short circuit photocurrent density; V_{oc}, open circuit photovoltage; FF, fill factor; η, total power conversion efficiency.

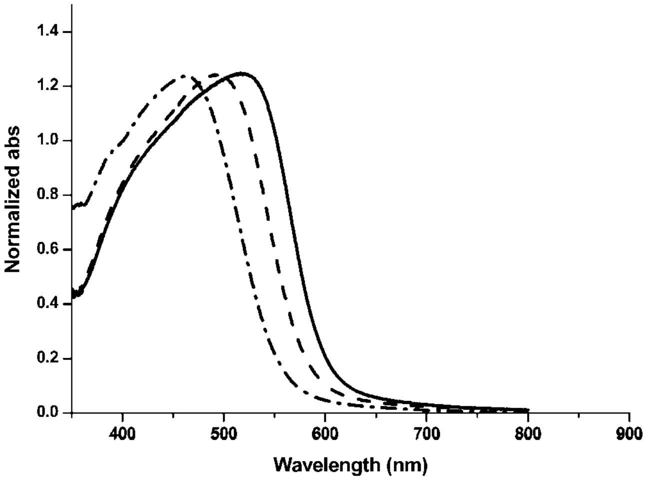

FIGURE 2. Absorption spectra of **JK-57** (dash dot line), **JK-58** (dash line), and **JK-59** (solid line) adsorbed on TiO_2 film.

in a detergent solution using an ultrasonic bath for 30 min and then rinsed with water and ethanol. Then, the plates were immersed in 40 mM $TiCl_4$ (aqueous) at 70 °C for 30 min and washed with water and ethanol. A transparent nanocrystalline layer was prepared on the FTO glass plates by using a doctor blade printing TiO_2 paste, which was then dried for 2 h at 25 °C. The TiO_2 electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The thickness of the transparent layer was measured by using an Alpha-step 250 surface profilometer. A paste containing 400 nm sized anatase particles was deposited by means of doctor blade printing to obtain the scattering layer and then dried for 2 h at 25 °C. The TiO_2 electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The resulting film was composed of a 10 μm thick transparent layer and a 4 μm thick scattering layer. The TiO_2 electrodes were treated again with $TiCl_4$ at 70 °C for 30 min and sintered at 500 °C for 30 min. Then, The TiO_2 electrodes were immersed into the dyes (**JK-57**, **JK-58**, and **JK-59**) solution (0.3 mM in THF) and kept at room temperature for 18 h. FTO plates for the counter electrodes were cleaned in an ultrasonic bath in H_2O, acetone, and 0.1 M aqueous HCl, subsequently. The counter electrodes were prepared by placing a drop of an H_2PtCl_6 solution (2 mg Pt in 1 mL ethanol) on an FTO plate and heating it (at 400 °C) for 15 min. The dye-adsorbed TiO_2 electrodes and the Pt counter electrodes were assembled into a sealed sandwich-type cell by heating with a Surlyn film as a spacer between the electrodes. A drop of the electrolyte solution was placed in the drilled hole of the counter electrode and was driven into the cell via vacuum backfilling. Finally, the hole was sealed using additional Surlyn and a cover glass (0.1 mm thickness). The electrolyte was then introduced into the cell, which was composed of 0.6 M 3-hexyl-1,2-dimethyl imidazolium iodide, 0.05 M iodine, 0.1 M LiI and 0.5 M *tert*-butylpyridine in acetonitrile. For photovoltaic measurement of the DSSCs, the cells were measured using 1000 W xenon light source.

Photoelectrochemical Measurement. The cells were measured using 1000 W xenon light source, whose power of an AM 1.5 solar simulator was calibrated by using KG5 filtered Si reference solar cell. The incident photon-to-current conversion efficiency (IPCE) spectra for the cells were measured on an IPCE measuring system.

1,4-Bis(isopentoxy)-2-methylbenzene (1). Yield: 59%. ^{1}H NMR ($CDCl_3$): δ 6.77 (d, J = 7.5 Hz, 1H), 6.76 (s, 1H), 6.69 (d, J = 7.5 Hz, 1H), 3.95 (t, J = 6.3 Hz, 2H), 3.94 (t, J = 6.6 Hz, 2H), 2.23 (s, 3H), 1.86 (m, 2H), 1.68 (m, 4H), 1.00 (d, J = 6.9 Hz, 6H), 0.99 (d, J = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.9, 151.6, 128.2, 117.8, 112.2, 111.7, 67.2, 66.9, 38.4, 38.3, 25.3, 25.2, 22.8, 22.7, 16.5. Anal. Calcd for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.01; H, 10.51.

2-(Bromomethyl)-1,4-bis(isopentoxy)benzene (2). Yield: 40%. ^{1}H NMR ($CDCl_3$): δ 6.90 (s, 1H), 6.80 (d, J = 1.2 Hz, 2H), 4.53 (s, 2H), 3.98 (t, J = 6.5 Hz, 2H), 3.95 (t, J = 6.5 Hz, 2H), 1.85 (m, 2H), 1.68 (q, J = 5.0 Hz, 2H), 1.63 (q, J = 5.0 Hz, 2H), 0.99 (d, J = 6.9 Hz, 6H), 0.97(d, J = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.9, 151.6, 127.2, 117.1, 115.9, 113.2, 67.5, 67.2, 38.3, 38.2, 29.2, 25.3, 25.2, 22.8, 22.7. Anal. Calcd for $C_{17}H_{27}BrO_2$: C, 59.48; H, 7.93. Found: C, 59.21; H, 7.81.

Diethyl (2,5-Bis(isopentoxy)phenyl)methylphosphonate (3). Yield: 75%. ^{1}H NMR ($CDCl_3$): δ 6.94 (s, 1H), 6.78 (d, J = 9.0 Hz, 1H), 6.75 (d, J = 9.0 Hz, 1H), 4.02 (t, J = 6.0 Hz, 4H), 3.94 (t, J = 5.0 Hz, 4H), 3.22 (d, J = 21.3 Hz, 2H), 1.81 (m, 2H), 1.65 (m, 4H), 1.26 (q, J = 6.9 Hz, 6H), 0.97 (d, J = 6.3 Hz, 6H), 0.96 (d, J = 6.3 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.9, 151.1, 121.5, 117.6, 114.0, 112.7, 67.2 (J_{c-p} = 39.2 Hz), 62.0, 61.9, 38.4, 38.3, 27.6, 25.2, 25.1, 22.8, 22.7, 16.5, 16.4. ^{31}P NMR ($CDCl_3$): δ 21.6. Anal. Calcd for $C_{21}H_{37}O_5P$: C, 62.98; H, 9.31. Found: C, 62.77; H, 9.10.

Diethyl (4-Formyl-2,5-bis(isopentoxy)phenyl)methylphosphonate (4). Yield: 75%. ^{1}H NMR ($CDCl_3$): δ 10.48 (s, 1H), 7.34 (s, 1H), 7.14 (s, 1H), 4.10 (m, 8H), 3.38 (d, J = 22.2 Hz, 2H), 1.89 (m, 2H), 1.78 (m, 4H), 1.30 (t, J = 7.2 Hz, 6H), 1.04 (d, J = 6.6 Hz, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 189.6, 155.9, 150.9, 129.6, 124.0, 116.3, 109.2, 67.4 (J_{C-P} = 28.1 Hz), 62.3, 62.2, 38.2, 38.0, 28.2, 25.3, 25.2, 22.7, 22.6, 16.5, 16.4. ^{31}P NMR ($CDCl_3$): δ 20.3. Anal. Calcd for $C_{22}H_{37}O_6P$: C, 61.67; H, 8.70. Found: C, 61.37; H, 8.56.

Diethyl (2,5-Bis(isopentoxy)-4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)methylphosphonate (5). Yield: 96%. ^{1}H NMR ($CDCl_3$): δ 7.09 (s, 1H), 6.90 (s, 1H), 5.66 (s, 1H), 3.95 (m, 8H), 3.69 (s, 2H), 3.58 (s, 2H), 3.17 (d, J = 21.6 Hz, 2H), 1.77 (m, 2H), 1.61 (m, 4H),

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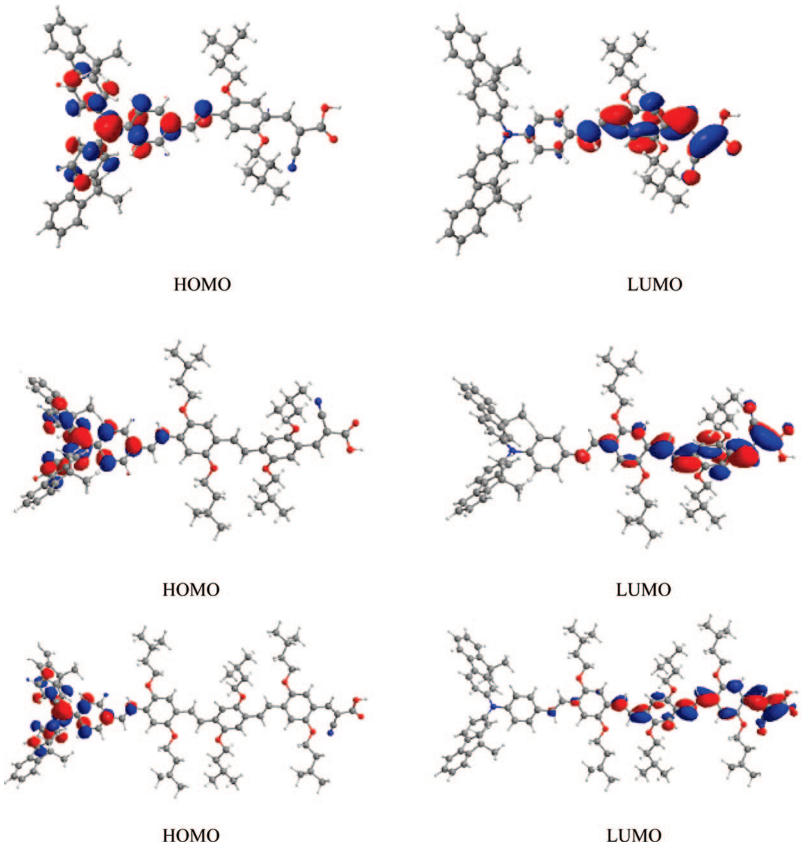

FIGURE 3. Molecular structures and the frontier molecular orbitals of the HOMO and LUMO calculated with B3LYP/3-21G* of (a) **JK-57**, (b) **JK-58**, and (c) **JK-59**.

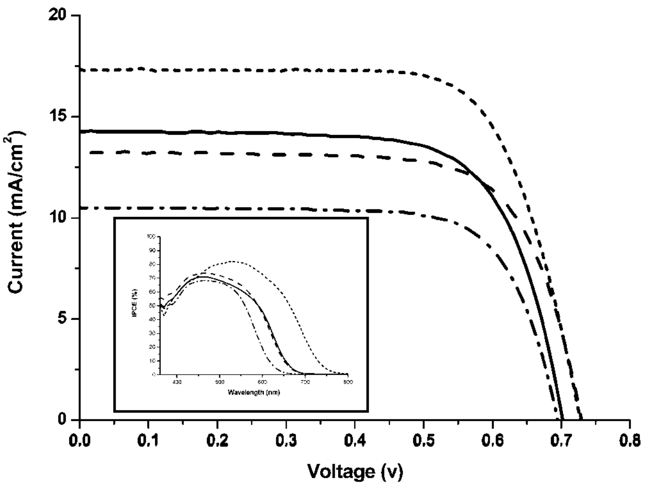

FIGURE 4. Photocurrent−voltage characteristics of representative TiO_2 electrodes sensitized with dye: **JK-57** (dash dot line), **JK-58** (dash line), **JK-59** (solid line), and **N719**(short dot). The inset shows the IPCE spectra of the DSSCs as a function of the wavelength of the light.

1.26 (s, 3H), 1.20 (t, $J = 7.0$ Hz, 6H), 0.90 (d, $J = 6.6$ Hz, 12H), 0.73 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 150.8, 149.7, 126.3, 121.5, 115.8, 110.1, 97.0, 67.8, 67.1, 61.8, 61.7, 38.2, 38.1, 30.2, 27.2, 25.4, 25.1, 25.0, 23.2, 22.6, 21.8, 16.4, 16.3. ^{31}P NMR ($CDCl_3$): δ 20.3. Anal. Calcd for $C_{27}H_{47}O_7P$: C, 63.01; H, 9.21. Found: C, 62.87; H, 9.10.

4-(*N,N*-Bis(9,9-dimethylfluoren-2-yl))benzaldehyde (7). Yield: 91%. ^1H NMR ($CDCl_3$): δ 9.84 (s, 1H), 7.73 ~ 7.18 (m, 18H), 1.43 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 190.6, 155.6, 153.8, 145.8, 138.7, 136.3, 131.5, 129.4, 127.3, 127.2, 125.0, 122.7, 121.1, 120.5, 120.1, 119.9, 47.1, 27.1. Anal. Calcd for $C_{37}H_{31}NO$: C, 87.89; H, 6.18. Found: C, 87.67; H, 6.09.

***N,N*-Bis(9,9-dimethylfluoren-2-yl)-2-(2,5-bis(isopentoxy)-4-styrylphenyl)-5,5-dimethyl-1,3-dioxane (8).** A stirred mixture of **7** (0.3 g, 0.60 mmol), **5** (0.34 g, 0.65 mmol), and potassium *tert*-butoxide (0.08 g, 0.72 mmol) was vacuum dried, and THF (25 mL) was added. The solution was refluxed for 6 h. THF was removed under reduced pressure. The crude mixture was redissolved in dichloromethane, washed with water, and dried with $MgSO_4$. The organic layer was removed in vacuo. The pure product **8** was obtained by silica gel chromatography (eluent MC/Hx = 1:2, $R_f = 0.3$) to afford **8** (0.24 g) in 80% yield. Mp: 197 °C. ^1H NMR ($CDCl_3$): δ 7.70−7.71 (m, 22H), 5.80 (s, 1H), 4.12 (t, $J = 6.3$ Hz, 2H), 4.10 (t, $J = 6.3$ Hz, 2H), 3.83 (d, $J = 10.2$ Hz, 2H), 3.73 (d, $J = 10.2$ Hz, 2H), 1.94 (m, 2H), 1.77 (m, 4H), 1.46 (s, 12H), 1.38 (s, 3H), 1.05 (d, $J = 5.1$ Hz, 6H), 1.04 (d, $J = 5.1$ Hz, 6H), 0.84 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.2, 153.7, 151.1, 150.0, 147.4, 139.1, 134.3, 129.8, 129.2, 128.3, 127.5, 127.1, 126.6, 124.0, 123.3, 122.6, 122.3, 120.8, 119.6, 118.8, 117.2, 111.3, 110.6, 97.2, 72.0, 68.2, 47.0, 38.4, 30.4, 27.2, 25.5, 23.4, 22.9, 22.2. Anal. Calcd for $C_{60}H_{67}NO_4$: C, 83.20; H, 7.80. Found: C, 83.02; H, 7.71.

***N,N*-Bis(9,9-dimethylfluoren-2-yl)-2-(2,5-bis(isopentoxy))-4-styrylbenzaldehyde (9).** THF (30 mL) and water (10 mL) were added to a flask containing **8** (0.3 0.35 mmol). Then, TFA (3 mL) was added to the solution. The resulting reaction mixture was stirred for 2 h at room temperature. The solution was quenched with saturated aqueous sodium bicarbonate and extracted with dichloromethane. The combined dichloromethane phases were then washed with aqueous sodium bicarbonate and dried with $MgSO_4$. The organic layer was removed in vacuo. The pure product **9** was obtained by silica chromatography (eluent MC/Hx = 1:1, $R_f = 0.3$) to afford **9** (0.24 g) in 80% yield. Mp: 220 °C. ^1H NMR ($CDCl_3$): δ 10.47 (s, 1H), 7.69 ~ 7.14 (m, 22H), 4.19 (t, $J = 6.6$ Hz, 2H), 4.11 (t, $J = 6.6$ Hz, 2H), 1.92 (m, 2H), 1.78 (m, 4H), 1.45 (s, 12H), 1.03 (d, *J*

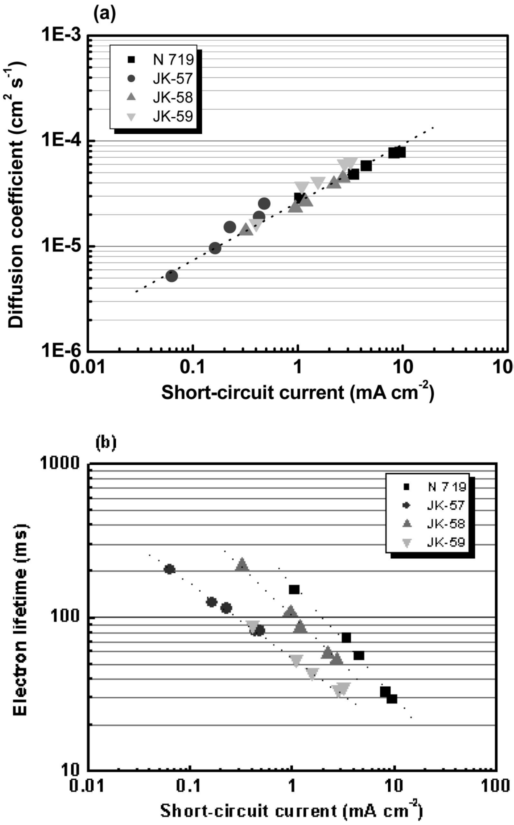

FIGURE 5. Electron diffusion coefficients (a) and lifetimes (b) in the photoelectrodes adsorbing different dyes (i.e., **N719**, **JK-57**, **JK-58**, and **JK-59**).

= 6.0 Hz, 6H), 1.02 (d, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 189.2, 156.4, 155.3, 153.7, 150.7, 148.3, 147.1, 139.0, 134.9, 134.7, 132.0, 131.3, 128.0, 127.2, 126.7, 124.0, 123.6, 123.5, 122.6, 121.1, 120.8, 119.6, 119.1, 110.3, 110.1, 67.7, 67.6, 47.0, 38.2, 38.1, 27.2, 25.5, 25.3, 22.8, 22.7. Anal. Calcd for $C_{55}H_{57}NO_3$: C, 84.69; H, 7.37. Found: C, 84.46; H, 7.31.

***N,N*-Bis(9,9-dimethylfluoren-2-yl)-2-(2,5-bis(isopentoxy)-4-styrylphenyl)-2-cyanoacrylic Acid (10, JK-57).** A mixture of **9** (0.224 g, 0.29 mmol) and cyanoacetic acid (0.03 g, 0.37 mmol) was vacuum-dried. MeCN (60 mL) and piperidine (0.026 mL, 0.29 mmol) were added to the mixture. The solution was refluxed for 6 h. After the solution was cooled, the organic layer was removed in vacuo. The pure product **10** was obtained by silica gel chrolmatography (eluent EA, R_f = 0.3) to afford **10** (0.12 g) in 50% yield. Mp: 238 °C. ^{1}H NMR (CDCl$_3$): δ 8.56 (s, 1H), 7.78 (s, 1H), 7.60−7.05 (m, 22H), 3.97 (t, J = 6.2 Hz, 2H), 3.89 (t, J = 6.2 Hz, 2H), 1.92 (m, 2H), 1.67 (m, 6H), 1.38 (s, 12H), 0.93 (d, J = 6.3 Hz, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 169.4, 155.2, 153.6, 153.2, 150.4, 147.9, 147.1, 146.8, 146.7, 139.0, 134.5, 132.5, 131.7, 130.9, 127.9, 127.1, 126.7, 123.7, 123.5, 122.6, 121.6, 120.8, 119.6, 118.9, 111.7, 109.4, 68.1, 67.6, 47.0, 38.2, 37.9, 27.2, 25.5, 25.4, 22.9, 22.8. Anal. Calcd for $C_{58}H_{58}N_2O_4$: C, 82.24; H, 6.90. Found: C, 82.02; H, 6.76.

***N,N*-Bis(9,9-dimethylfluoren-2-yl)-2-(4-(2,5-bis(isopentoxy)-4-styrylstyryl)-2,5-bis(isopentoxy)phenyl)-5,5-dimethyl-1,3-dioxane (11).** A stirred mixture of **9** (0.645 g, 0.83 mmol), **5** (0.43 g, 0.83 mmol), and potassium *tert*-butoxide (0.12 g, 1.00 mmol) was vacuum-dried, and THF (35 mL) was added. The solution was refluxed for 6 h. THF was removed under reduced pressure. The crude mixture was redissolved in dichloromethane, washed with water, and dried with MgSO$_4$. The organic layer was removed in vacuo. The pure product **11** was obtained by silica gel chromatography (eluent MC/Hx = 1:1, R_f = 0.4) to afford **11** (0.66 g) in 70% yield. Mp: 200 °C. ^{1}H NMR (CDCl$_3$): δ 7.67−7.11 (m, 26H), 5.76 (s, 1H), 4.09 (m, 8H), 3.80 (d, J = 10.2 Hz, 2H), 3.70 (d, J = 10.2 Hz, 2H), 1.93 (m, 4H), 1.76 (m, 8H), 1.43 (s, 12H), 1.35 (s, 3H), 1.02 (d, J = 6.3 Hz, 24H), 0.82 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 155.2, 154.5, 153.7, 151.1, 150.8, 150.5, 147.4, 147.1, 139.1, 134.4, 133.6, 131.3, 128.6, 128.3, 127.5, 127.1, 126.9, 126.3, 124.0, 123.7, 123.4, 122.6, 122.3, 121.9, 120.7, 119.6, 118.8, 111.5, 111.3, 110.6, 110.4, 97.3, 68.0, 67.9, 67.6, 47.0, 38.5, 38.4, 38.3, 30.5, 27.2, 25.6, 25.5, 25.3, 23.4, 22.9, 22.8, 22.7, 22.1. Anal. Calcd for $C_{78}H_{93}NO_6$: C, 82.14; H, 8.22. Found: C, 81.92; H, 8.07.

***N,N*-Bis(9,9-dimethylfluoren-2-yl)-2-(4-(2,5-bis(isopentoxy)-4-styrylstyryl)-2,5-bis(isopentoxy)phenyl)benzaldehyde (12).** THF (30 mL) and water (10 mL) were added to a flask containing **11** (0.36 g, 0.32 mmol). Then TFA (5 mL) was added to the solution. The resulting reaction mixture was stirred for 2 h at room temperature. The solution was quenched with saturated aqueous sodium bicarbonate and extracted with dichloromethane. The combined dichloromethane phases were then washed with aqueous sodium bicarbonate and dried with MgSO$_4$. The organic layer was removed in vacuo. The pure product **12** was obtained by silica gel chromatography (eluent MC/Hx = 1:1, R_f = 0.3) to afford **12** (0.3 g) in 90% yield. Mp: 254 °C. ^{1}H NMR (CDCl$_3$): δ 10.47 (s, 1H), 7.68 ~ 7.12 (m, 26H), 7.67 (t, J = 5.7 Hz, 2H), 7.62 (s, 2H), 7.55 (s, 2H), 7.49 (d, J = 8.4 Hz, 4H), 7.43 (d, J = 19.5 Hz, 1H), 7.40 (d, J = 18.6 Hz, 1H), 7.34 (d, J = 7.5 Hz, 2H), 7.31 (m, 4H), 7.30 (d, J = 8.4 Hz, 2H), 7.28 (s, 2H), 7.22 (d, J = 18 Hz, 1H), 7.20 (d, J = 18.9 Hz, 1H), 4.15 (m, 8H), 1.95 (m, 4H), 1.79 (m, 8H), 1.44 (s, 12H), 1.05 (d, J = 5.4 Hz, 12H), 1.04 (d, J = 5.7 Hz, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 189.3, 156.4, 155.2, 153.7, 151.5, 151.1, 150.8, 147.6, 147.3, 139.1, 135.3, 134.5, 132.2, 128.9, 128.2, 127.6, 127.1, 126.9, 126.7, 126.3, 124.1, 123.9, 123.4, 122.6, 122.3, 121.9, 120.8, 119.6, 118.9, 110.5, 110.3, 110.2, 110.1, 67.9, 67.7, 67.6, 47.0, 38.4, 38.2, 38.1, 27.2, 25.6, 25.5, 25.3, 22.9, 22.8, 22.7. Anal. Calcd for $C_{73}H_{83}NO_5$: C, 83.15; H, 7.93. Found: C, 82.89; H, 7.81.

***N,N*-Bis(9,9-dimethylfluoren-2-yl)-2-(4-(2,5-bis(isopentoxy)-4-styrylstyryl)-2,5-bis-(isopentoxy)phenyl)-2-cyanoacrylic Acid (13, JK-58).** A mixture of **12** (0.245 g, 0.23 mmol) and cyanoacetic acid (0.026 g, 0.30 mmol) was vacuum-dried, and MeCN (60 mL) and piperidine (0.023 mL, 0.23mmol) were added. The solution was refluxed for 6 h. After the solution was cooled, the organic layer was removed in vacuo. The pure product **13** was obtained by silica gel chromatography (eluent EA, R_f = 0.3) to afford **13** (0.12 g) in 50% yield. Mp: 272 °C. ^{1}H NMR (CDCl$_3$): δ 8.65 (s, 1H), 7.84−7.06 (m, 26H), 4.02 (m, 8H), 1.89 (m, 4H), 1.74 (m, 8H), 1.41 (s, 12H), 0.98 (br s, 24H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 169.4, 155.2, 153.7, 153.2, 151.3, 150.3, 147.5, 147.3, 139.1, 134.4, 132.9, 132.4, 128.6, 127.7, 127.6, 127.1, 126.6, 125.4, 124.0, 123.4, 122.6, 122.2, 122.1, 121.0, 120.7, 119.6, 118.8, 111.8, 110.1, 108.9, 105.0, 67.9, 67.7, 67.6, 47.0, 38.4, 38.2, 37.8, 27.2, 25.7, 25.6, 25.4, 23.0, 22.9, 22.8. Anal. Calcd for $C_{76}H_{84}N_2O_6$: C, 81.39; H, 7.55. Found: C, 81.11; H, 7.41.

***N,N*-Bis(9,9-dimethylfluoren-2-yl)-2-(4-(4-(2,5-bis(isopentoxy)-4-styrylstyryl)-2,5-bis(isopentoxy)styryl)-2,5-bis(isopentoxy)phenyl)-5,5-dimethyl-1,3-dioxane (14).** A stirred mixture of **12** (0.5 g, 0.47 mmol), **5** (0.27 g, 0.52 mmol), and potassium *tert*-butoxide (0.064 g, 0.57 mmol) was vacuum-dried and THF (35 mL) was added. The solution was refluxed for 6 h. THF was removed under reduced pressure. The crude mixture was redissolved in dichloromethane, washed with water, and dried with MgSO$_4$. The organic layer was removed in *vacuo*. The pure product **14** was obtained by silica gel chromatography (eluent MC/Hx = 1: 1, R_f = 0.4) to afford **14** (0.47 g) in 70% yield. Mp: 220 °C. ^{1}H NMR (CDCl$_3$): δ 7.67−7.11 (m, 28H), 5.75 (s, 1H), 4.10 (m, 12H), 3.80 (d, J = 10.2 Hz, 2H), 3.69 (d, J = 10.2 Hz, 2H), 1.94 (m, 6H), 1.79 (m, 12H), 1.43 (s, 12H), 1.35 (s, 3H), 1.01 (m, 36H), 0.81 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 155.2, 153.7, 152.1, 151.5, 151.2, 151.1, 150.4, 150.1, 147.4, 147.2, 139.1, 136.2, 135.2, 134.4, 132.4, 128.6, 128.2, 127.5, 127.1, 127.0, 126.6, 126.3, 126.1, 124.0, 123.4, 123.3, 123.1, 122.6, 122.4, 122.1, 120.7, 119.6, 118.8, 118.1, 117.2, 111.4, 110.5, 110.3, 110.2, 97.2, 78.0, 68.0, 67.9, 67.7, 67.6, 67.5, 47.0, 38.5, 38.2, 38.1, 30.5, 27.2, 25.6, 25.5, 25.4, 23.4, 22.9, 22.8, 22.7, 22.1. Anal. Calcd for $C_{96}H_{119}NO_8$: C, 81.49; H, 8.48. Found: C, 81.19; H, 8.32.

***N,N*-Bis(9,9-dimethylfluoren-2-yl)-4-(4-(2,5-bis(isopentoxy)-4-styrylstyryl)-2,5-bis-(isopentoxy)styryl)-2,5-bis(isopentoxy)benzaldehyde (15).** THF (30 mL) and water (10 mL) were added to a flask containing **14** (0.4 g, 0.28 mmol). Then TFA (5 mL) was added to the solution. The resulting reaction mixture was stirred for 2 h at room temperature. The solution was quenched with saturated aqueous sodium bicarbonate and extracted with dichloromethane. The combined dichloromethane phase was then washed with aqueous sodium bicarbonate and dried with $MgSO_4$. The organic layer was removed in vacuo. The pure product **15** was obtained by silica gel chromatography (eluent MC/Hx = 1:1, $R_f = 0.3$) to afford **15** (0.34 g) in 91% yield. Mp: 257 °C. ^{1}H NMR ($CDCl_3$): δ 10.46 (s, 1H), 7.68−7.12 (m, 30H), 4.11 (m, 12H), 1.94 (m, 6H), 1.79 (m, 12H), 1.43 (s, 12H), 1.03 (m, 36H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 189.3, 156.4, 155.2, 153.7, 151.5, 151.2, 151.2, 151.1, 150.8, 147.5, 147.3, 139.1, 135.3, 134.4, 132.4, 128.9, 128.6, 128.4, 127.5, 127.4, 127.2, 127.0, 126.7, 126.5, 124.2, 124.0, 123.7, 123.4, 122.9, 122.6, 122.4, 122.1, 120.8, 119.6, 118.8, 110.6, 110.5, 110.3, 110.2, 68.1, 68.0, 67.8, 67.7, 67.6, 47.0, 38.4, 38.2, 38.2, 27.2, 25.6, 25.5, 25.3, 23.0, 22.9, 22.8, 14.3. Anal. Calcd for $C_{91}H_{109}NO_7$: C, 82.25; H, 8.27. Found: C, 82.02; H, 8.09.

***N,N*-Bis(9,9-dimethylfluoren-2-yl)-2-(4-(4-(2,5-bis(isopentoxy)-4-styrylstyryl)-2,5-bis(isopentoxy)styryl)-2,5-bis(isopentoxy)phenyl)-2-cyanoacrylic Acid (16, JK-59).** A mixture of **15** (0.35 g, 0.26 mmol) and cyanoacetic acid (0.03 g, 0.34 mmol) was vacuum-dried, and MeCN (60 mL) and piperidine (0.027 mL, 0.26 mmol) were added. The solution was refluxed for 6 h. After the solution was cooled, the organic layer was removed in vacuo. The pure product **16** was obtained by silica gel chromatography (eluent EA, $R_f = 0.3$) to afford **16** (0.18 g) in 50% yield. Mp: 274 °C. ^{1}H NMR ($CDCl_3$): δ 8.66 (s, 1H), 7.85−7.10 (m, 31H), 4.05 (m, 12H), 1.92 (m, 6H), 1.75 (m, 12H), 1.41 (s, 12H), 0.96 (m, 36H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 186.2, 173.8, 169.9, 168.9, 166.1, 163.4, 155.2, 153.7, 153.3, 151.4, 151.1, 150.4, 147.3, 142.3, 141.7, 139.1, 138.6, 137.9, 134.3, 133.2, 132.5, 128.2, 127.5, 127.2, 126.6, 125.7, 125.1, 124.0, 123.3, 122.9, 122.6, 122.1, 120.8, 119.6, 118.8, 111.7, 110.3, 110.0, 109.2, 101.7, 68.1, 68.0, 67.8, 67.7, 67.6, 47.0, 38.4, 38.2, 38.0, 27.2, 25.6, 25.5, 25.4, 22.9, 22.8, 22.7. Anal. Calcd for $C_{94}H_{110}N_2O_8$: C, 80.88; H, 7.94. Found: C, 80.59; H, 7.83.

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Supporting Information Available: ^{1}H and ^{13}C NMR for all compounds and ^{31}P NMR spectra for compounds **4−6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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