Supplementary Information

Six-Member-Ring Photocyclization in Phenyl Substituted *p*-Phenylenevinylene Derivatives: a Potential Factor of Instability in Conjugated Polymers

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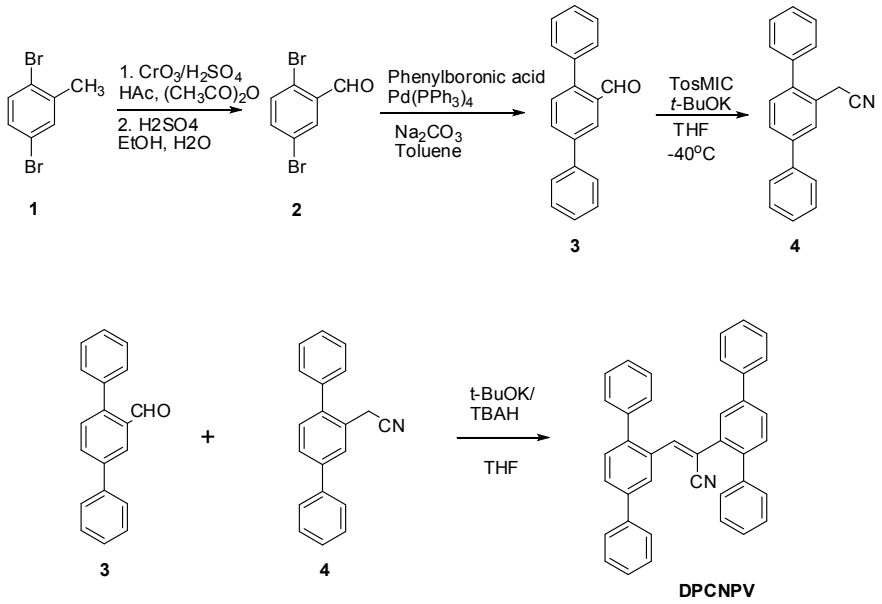
SI. General experiments

All chemicals and reagents were used as received from Aldrich, TCI and Acros Chemical Co. unless specified otherwise. All solvents were carefully dried and purified before use. All manipulations involving air-sensitive reagents were performed under a dry argon atmosphere. NMR (300 MHz) spectra were obtained using a Bruker 300M Hz spectrometer with tetramethylsilane as an internal standard. C, H, N elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). The GC-mass spectra were measured by Finnigan TRACE MS. IR spectra were recorded on Perkin-Elmer spectrophotometer in the 4000-400 cm^{-1} region using a powered sample on a KBr plate. UV-visible absorption spectra were recorded on a HP 8453 UV-vis spectrophotometer. PL spectra were obtained with a Fluorolog JY luminescence spectrometer. The ground-state geometries of *cis*-/*trans*-conformation and anti/syn-configuration in DPCNPV were optimized at the B3LYP level of theory using the basis set of 6-31G (d, p) without symmetry restrictions, which is carried out in the Gaussian 09 program package.

SII. Synthesis



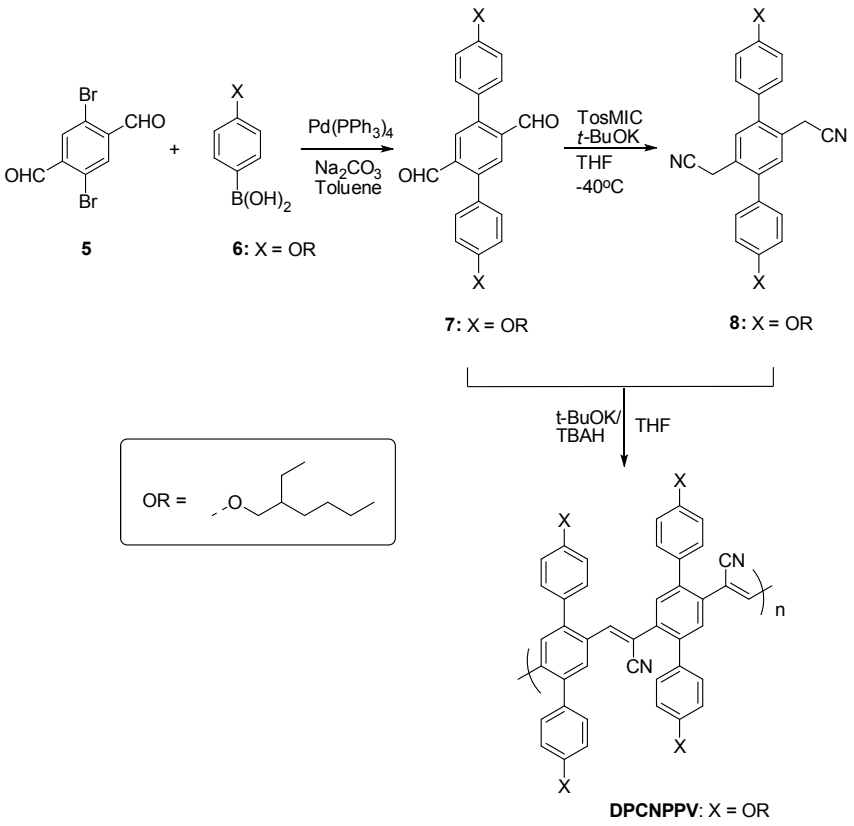
Scheme S1. Synthesis of model compounds DPCNPV.

2,5-dibromobenzaldehyde(2). Sulfuric acid (7 mL) was added dropwise to a suspension containing 1,4-dibromo-2-methylbenzene (4.0 g), acetic acid (10 mL) and acetic anhydride (20 mL) at 0°C. CrO_3 (3 g) was then added to the mixture in portions. The resulting mixture was stirred vigorously at this temperature for a further 5 h until the reaction was completed. The greenish slurry was poured into ice-water and filtered. The white solid was washed with cold methanol. The diacetate was then hydrolyzed by refluxing with a mixture of water (20 mL), ethanol (20 mL) and sulfuric acid (2 mL) for 5 h. After the mixture was cooled to room temperature, the pale yellow product was separated by filtration. The crude product was purified by recrystallization from chloroform. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$, TMS, ppm): δ = 10.29 (s, 1H; CHO), 8.03 (d, 1H; PhH), 7.57 (dd, 1H; PhH), 7.53 (s, 3H; CH_3).

[1,1':4',1''-terphenyl]-2'-carbaldehyde (3). Newly distilled toluene (6 mL) and Na_2CO_3aqueous solution (1.3 mL, 2 M) was added to a two-necked round bottom flask containing **6** (2 mmol), phenylboronic acid (5 mmol) and $Pd(PPh_3)_4$ (0.096 mmol) under nitrogen. The mixture was refluxed at 80 °C for 36 h. After cooled to room temperature the reaction mixture was poured into water (30 mL) and extracted with dichloromethane (3×10 mL), then dried over anhydrous $MgSO_4$overnight. After filtration the solvent was removed with rotary evaporator. The crude product was purified by chromatographyusing silica gel (mixture of hexane and ethyl acetate (v/v = 10:1) as the eluent) to give the target compound as white solid (315mg, yield 61%). ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$, TMS, ppm): δ = 10.05 (s, 1H; CHO), 8.27 (d, 1H; PhH), 7.89 (dd, 1H; PhH), 7.69 (d, 2H; PhH), 7.54 (d, 1H; PhH), 7.51-7.38 (m, 8H; PhH).

[1,1':4',1''-terphenyl]-2'-carbonitrile(4).A solution of tosylmethyl isocyanide (TosMIC) (1.1 mmol) in anhydrous THF (1.7 mL) was slowly added to a solution of *t*-BuOK (2.3 mmol) in anhydrous THF (5.1 mL) under nitrogen with stirring. The resulting mixture was cooled at -40 °C and a solution containing **7** (0.5 mmol) in anhydrous THF (1.7 mL) was slowly added. The mixture was stirred at -40 °C for 2 h followed by the addition of methanol (7 mL). The solution was heated at 80 °C for 20 min and cooled to room temperature. The solvent was removed under reduced pressure, and then glacial acetic acid (1 mL) was added to the resulting mixture. Then, water (20 mL) was added and the crude product was extracted with dichloromethane (3×10 mL). The combined organic layer was dried over anhydrous $MgSO_4$overnight. After filtration the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, mixture of hexane and ethyl acetate (v/v= 5:1) as the eluent) to provide a white solid (54mg, yield 40%). ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$, TMS, ppm): δ = 7.77 (s, 1H; PhH), 7.66 (d, 2H; PhH), 7.63 (d, 1H; PhH), 7.49 (t, 4H; PhH), 7.43-7.33 (m, 5H; PhH)，3.71 (s, 2H; CH_2CN).

DPCNPV. *t*-BuOK (0.02 mmol) and TBAH (0.02 mmol, 1 M in methanol) was added fleetly to a solution of7 (0.2 mmol) and 8 (0.2 mmol) in *t*-BuOH (1.2 mL) and THF (0.4 mL) at 50 °C under nitrogen with rigorous exclusion of light. 40 min later, the solution was poured into a mixture of acetic acid and methanol. The precipitate was filtered and washed with plenty of water and methanol to give the white solid (yield 62%).^{1}H NMR (500 MHz, 25 °C, $CDCl_3$, TMS, ppm): δ = 8.29 (s, 1H), 7.72 (d, 1H; PhH), 7.69 (m, 3H; PhH), 7.61 (m, 3H; PhH), 7.49-7.37 (m, 16H; PhH), 7.32 (d, 2H; PhH), 7.24 (s, 1H; PhH). ^{13}C NMR (125 MHz, 25 °C, $CDCl_3$, TMS, ppm): δ = 147.28, 141.85, 141.16, 141.04, 140.54, 140.48, 140.18, 140.03, 135.17, 132.81, 131.58, 131.01, 130.20, 129.82, 129.40, 129.34, 129.04, 128.91, 128.85, 128.21, 128.13, 127.69, 127.48, 118.05, 113.89; FT-IR (KBr pellet, cm^{-1}): 3073, 3058, 3045, 3025, 2223, 1598, 1575, 1475, 1450, 1392, 1338, 1211, 1184, 1159, 1074, 1025, 1008, 917, 902, 833, 755, 734, 698; MALDI-TOF MS: m/z = 508.9($[M]^+$). Calcd for $C_{39}H_{27}N$: 509.2.



Scheme S2. Synthesis of DPCNPPV.

4,4''-bis((2-ethylhexyl)oxy)-[1,1':4',1''-terphenyl]-2',5'-dicarbaldehyde(7). Newly distilled toluene (4.2 mL) and Na_2CO_3 aqueous solution (0.9 mL, 2 M) was added to a two-necked round bottom flask containing **1** (1.4 mmol), **2** (3.2 mmol) and $Pd(PPh_3)_4$ (0.096 mmol) under nitrogen. The mixture was refluxed at 80 °C for 36 h. After cooled to room temperature, the reaction mixture was poured into water (20 mL) and extracted with dichloromethane (3×10 mL), then the organic layer was separated and dried over aqueous $MgSO_4$ and the solvent was removed using rotary evaporator. The resulting solid was purified by chromatography using silica gel to give the target compound **3** (608 mg, yield 80%). ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$, TMS, ppm): δ = 10.09 (s, 2H; CHO), 8.07 (s, 2H; PhH), 7.35 (d, 4H; PhH), 7.04 (d, 4H; PhH), 3.92 (d, 4H; OCH), 1.77 (m, 2H; CH), 1.57-1.33 (m, 16H; CH_2), 0.97-0.91 (m,12H; CH_3). Anal. calcd for $C_{36}H_{46}O_4$: C, 79.67; H, 8.54. Found: C, 79.60; H, 8.53.

4,4''-bis((2-ethylhexyl)oxy)-[1,1':4',1''-terphenyl]-2',5'-dicarbonitrile(8). A solution of tosylmethyl isocyanide (TosMIC) (1.1 mmol) in anhydrous THF (1.7 mL) was slowly added under nitrogen to a solution of *t*-BuOK (2.3 mmol) in anhydrous THF (5.1 mL). The resulting mixture was cooled to -40 °C, and then a solution of **3** (0.5 mmol) in anhydrous THF (1.7 mL) was added dropwise. The mixture was stirred at -40 °C for 2 h followed by the addition of methanol (7 mL). The solution was heated at 80 °C for 20 min, and then cooled to room temperature. The solvent was removed under reduced pressure, and

glacial acetic acid (1 mL) was added to the resulting mixture. Then, water (20 mL) was added and the crude product was extracted with dichloromethane (3×10 mL). The combined organic layer was dried over aqueous $MgSO_4$ overnight, and after filtration the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, mixture of ethyl acetate and hexane (v/v = 1:3) as the eluent) to provide white solid (85mg, yield 30%). ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$, TMS, ppm): δ = 7.44 (s, 2H; PhH), 7.24 (d, 4H; PhH), 7.01 (d, 4H; PhH), 3.91 (s, 4H; OCH), 3.67 (s, 4H; CH_2CN), 1.77 (m, 2H; CH), 1.57-1.33 (m, 16H; CH_2), 0.97-0.91 (m, 12H; CH_3). Anal. calcd for $C_{38}H_{48}N_2O_2$: C, 80.81; H, 8.57; N, 4.96. Found: C, 80.85; H, 8.55; N, 4.85.

DPCNPPV. Potassium tertbutoxide (0.01 mmol) and TBAH (0.01 mmol，1 M in methanol) was added fleetly to a solution of **3** (0.1 mmol) and **4** (0.1 mmol) in tertiary butanol (0.75 mL) and tetrahydrofuran (0.25 mL) at 50 °C under nitrogen with rigorous exclusion of light. 40 min later, the solution was poured into a mixture of acetic acid and methanol. After filtered, the filter cake was washed by methanol with soxhlet extractor in exclusion of light for 24 h to get target compound. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$, TMS, ppm): δ = 8.04-6.81 (22H), 3.85 (8H), 1.74-0.89 (60H); FT-IR (KBr pellet, cm^{-1}): 3036, 2957, 2926, 2871, 2858, 2214, 1689, 1608, 1574, 1520, 1467, 1422, 1382, 1292, 1245, 1176, 1110, 1030, 908, 830. GPC: Mn 12837, Mw 21137, PDI 1.6.

SIII. ^{1}H-NMR Spectra of DPCNPPV before and after Photo-Irradiation

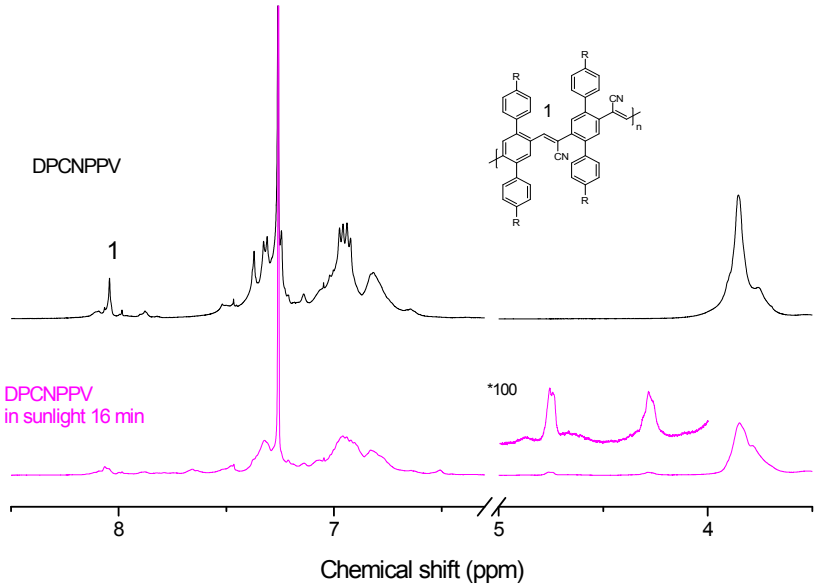


Figure S1 ^{1}H-NMR spectra of DPCNPPV before and after photo-irradiation.

SIV. UV-vis and PL Spectra of DPCNPPV and degraded DPCNPPV in films

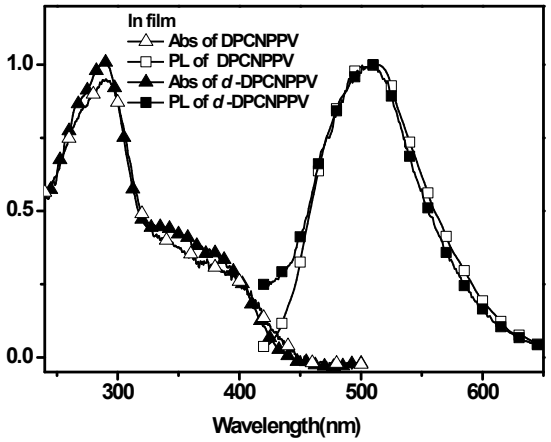


Figure S2 UV-vis and PL Spectra of DPCNPPV and degraded DPCNPPV (*d*-DPCNPPV degraded in solution under sunlight for 16 min before spin-coating) in films

SV. Single crystal X-ray diffraction data

Single crystal of DPCNPV and α-DHPD were prepared by vaporizing chloroform slowly at room temperature under rigorous exclusion of light. The diffraction experiments were carried out on a Rigaku R-AXIS RAPID diffractometer equipped with a Mo-Kα and Control Software using the RAPID AUTO at 293 (±2) °C. Empirical absorption corrections were applied automatically. The structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS v. 5.1 programs, respectively. The space groups were determined from the systematic absences and their correctness was confined by successful solution and refinement of structures. Anisotropic thermal parameters were refined for all the non-hydrogen atoms. The hydrogen atoms were added in idealized position and refined with isotropic displacement. Crystal date refinement conditions and experimental details are tabulated in table S1.

CCDC 1426125 and 1423134 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Table S1 Crystallographic data and structure refinement for DPCNPV and α-DHPD.

Identificationcode	**DPCNPV**	**α-DHPD**
Empirical formula	$C_{39}H_{27}N$	$C_{39}H_{27}N$
Formula weight	509.62	509.62
T/K	293(2)	293(2)
Crystal system	Monoclinic	Triclinic
space group	P2(1)/c	P-1
a/Å	14.249(5)	10.698(2)
b/Å	11.262(5)	13.920(3)
c/Å	17.886(6)	14.187(3)
α/°	90	115.44(3)
β/°	104.314(11)	109.10(3)
γ/°	90	95.49(3)
V/Å^3	2781.1(18)	1732.2(6)
Z	4	2
Density/Mg/m^3	1.217	1.240
M(Mo Kα)/mm^{-1}	0.070	0.331
θrange/°	3.04-27.49	3.23-27.48
Reflections collected	26273	17039
Independent reflections	6340	7786
R(int)	0.1244	0.0405
GOF	0.944	1.129
R1[I>2σ(I)]	0.0685	0.1010
wR2[I>2σ(I)]	0.1132	0.2919
R1(all data)	0.2170	0.1509
wR2(all data)	0.1545	0.3362
Final diff. ρ_{max}(e. Å^{-3})	0.134,-0.159	0.842,-0.863