Supporting Information

Understanding Molecular Gelation Processes of Heteroatomic Conjugated Polymers for Stable Blue Polymer Light-Emitting Diodes

Jin-Yi Lin^{a, b, c} Bin Liu, ^b Meng-Na Yu, ^b Chang-Jin Ou, ^aZhen-Feng Lei, ^b Xu-Hua Wang, ^c

Ling-Hai Xie, *^b Wen-Sai Zhu, ^a Hai-Feng Ling, ^b Xin-Wen Zhang, *^bPaul N. Stavrinou, ^d Jian-Pu Wang, ^a Donal D. C. Bradley, *^e Wei Huang^{*a, b}

^aKey Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM),

Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing

Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211816, China.

^bCenter for Molecular Systems and Organic Devices (CMSOD), Key Laboratory for Organic

Electronics and Information Displays & Institute of Advanced Materials (IAM), Jiangsu

National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University

of Posts & Telecommunications (NUPT), 9 Wenyuan Road, Nanjing 210023, China.

^cDepartment of Physics and Centre for Plastic Electronics, The Blackett Laboratory, Imperial College London, Prince Consort Road, London SW7 2AZ, UK

^dDepartment of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PD,

UK

^eDepartments of Mathematical, Physical and Life Sciences Division, University of Oxford, 9 Parks Road, Oxford OX1 3PD, UK.

Experimental Section.

Chemicals and Materials. Alumina (Al₂O₃), 2,2'-bipyridine, 1,5-cyclooctadiene (COD), bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)₂), hydrazine hydrate and all solvents were purchased from Aldrich or J&K Chemicals and used without further purification. Anhydrous Tetrahydrofuran (THF) (HPLC grade) was collected from Solvent Purification Systems (Innovative Technology, Inc.). The 4,5-diaza-2,7-dibromo-9,9-di-n-octyl-fluorene (DBrDAF8), was synthesized with 50% yield according to published procedures.^{1,2} Anhydrous chloroform was pre-dried over molecular sieves. N,N-Dimethylformamide (DMF) solvent was dried over calcium hydride (CaH) and distilled under a dry nitrogen atmosphere immediately prior to use. The other solvents were distilled under a dry nitrogen atmosphere immediately prior to use.

Characterization. ¹H-NMR was recorded on a Bruker 400 MHz spectrometer in CDCl₃ or d8toluene with tetramethylsilane (TMS) as the internal standard. Gel permeation chromatography (GPC) analysis was performed on a HP1100 HPLC system equipped with 7911GP-502 and GP NXC columns using polystyrene as a standard and tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min. Absorption spectra were measured with a Shimadzu UV-3600 spectrometer at room temperature, and emission spectra were recorded on a Shimadzu RF-5301(PC)S luminescence spectrometer. Quartz cells, with a length of 10 mm, were used to measure the spectra of solution, while cells of 1 mm length were used to measure the spectra of gels. The low temperature emission spectra were recorded on a Hitachi F-4600 luminescence spectrometer, and the film samples were added into a quartz tube and dipped into a quartz container filled with liquid nitrogen. The excitation wavelength was 390 nm for PL, and 465 nm for PLE. The AFM images of polyfluorene films spin-coated on silicon chips were obtained by using a Dimension 3100 (Veeco, CA) in tapping model with a Si tip (resonance frequency: 320 kHz; spring constant: 42 N m-1) at a scanning rate of 1 Hz. Film thickness measurements were performed using a BrukerDektak XT stylusprofiler. The fluorescence lifetimes were measured using a Coherent mode-locked Ti: Sapphirelaser system with the wavelength of 390 nm and 150 fs laser pulses to excite the samples. Emission from the samples was collected at a back scattering angle of 150° by a pair of lenses and directed to an OptronisOptoscopeTM streak camera, with a temporal resolution of 6 ps. GIXD measurements were performed on Beamline 7.3.3 at the Advanced Light Source (ALS) atthe Lawrence Berkeley National Laboratory.

Preparation of PF8-*co***-DAF8 solutions, gels and films.** The preparation of PF8-*co*-DAF8 solutions was carried out by dissolving the polymer in the organic solvents spontaneously overnight. Various solvents in the case of PF8-*co*-DAF8 gels were prepared by agitating their solutions at 60 °C for 10 min, where a macroscopically homogeneous solution was obtained once fully dissolved. The PF8-*co*-DAF8-based gels were prepared by aging the solutions with different concentrations at room temperature. In analyzing the critical concentration of gels in various solvents, 5 mg of PF8-*co*-DAF8 and 50 μ L of solvents were successively added into a sealed glass via ltowork out the solution concentration threshold of a gel formation.

Pristine films of polymers for UV-PL spectra, AFM and GIXD analysis, were spin-coated on quartz (For optical analysis) or silican (For GIXD analysis) substrates from their toluene or CHCl₃ solution (various concentration) using KW-4A (from the institute of micro-electronics of Chinese Academy of Science) at 1500 rpm for 30s. The PF8-*co*-DAF8 (20%) films were spin-coated from the solutions in pristine toluene or CHCl₃ solution with the concentration of 8 mg/mL and 5 mg/mL. Film thicknesses were measured to be 70~80 nm. Low temperature for obtaining PL and PLE spectra is about 77 K.

Preparation of PF8-*co***-DAF8-based PLEDs.** A polymer light emitting diode was made from PF8-*co*-DAF8 or PF8 as an emitter with the device structure of indium tinoxide (ITO)/poly(3,4-ethylenedioxy thiophene):poly(styrene sulfonicacid) (PEDOT:PSS)/ PF8-*co*-DAF8 or PF8/TPBi/LiF/Al. A thin hole-injection layer (20 nm) of PEDOT: PSS was spin-coated on the

transparent conductive ITO at a spin speed of 1000 rpm for 78 s. After baking at 120 °C for 15 min in an oven, the emissive polymer layer was coated on the top of the PEDOT: PSS layer from its fresh solutions. Finally, a 20 nm electron transport layer of TPBi and LiF (0.8 nm)/Al (100 nm) were deposited by thermal evaporation. The current-voltage luminescence characteristics from the devices were recorded using a Keithley source meter (model 2602) and a PR655 spectroradiometer. EL spectra and CIE coordinates of the devices were recorded using a Spectra Scan PR655 spectro radiometer. All the devices were characterized without encapsulation under ambient conditions at room temperature. The emission area of a pixel is 12 mm².

Poly((9,9-dioctyl-fluorene)-*co*-**(9,9-dioctyldiazafluoren-2,7-yl)** (**PF8**-*co*-**DAF8**). Various ratios of DBrF8 and DBrDAF8 (Total: 0.76 mmol) were added to mixture of DMF (10 mL) and toluene (10 mL) solution containing Ni(COD)₂ (0.50 g, 1.82 mmol), 1,5-cyclooctadiene (COD) (0.24 mL, 1.82 mmol) and 2,2'-bipyridine (0.28 g, 1.82 mmol) in a 50 mL Schlenktube under argon, respectively. The reaction mixture was stirred for 96 hrs at 85 °C to obtain a dark blue solution. Then, bromobenzene was added to the solution for a final reaction. After the final product cooled to room temperature, 10 ml of THF and 1.0 mL of hytrazine hydrate were added for quenching reaction. The precipitate was separated by filtration. The solution had further purification subjected to Al₂O₃ column chromatography eluting with THF to afford PF8-*co*-DAF8 for the sp² nitrogen substitute fractions of 20%, 30% and 50% with the weights and yields of (0.23 g, 78.31%), (0.25 g, 84.41%) and (0.21 g, 72.61%), respectively. GPC: M_n of 6.99 × 10⁴ with the PDI of 1.42 for 20%, M_n of 6.69 × 10⁴ with the PDI of 1.46 for 30% and M_n of 5.49 × 10⁴ with the PDI of 1.88 for 50% PF8-*co*-DAF8 polymers. ¹H NMR (400 MHz, CDCl₃, 298 K) δ (ppm): 9.06 (s, ArH), 8.05-7.69 (m, ArH), 2.16-2.13 (m, CH₂), 1.58-1.57 (m, CH₂), 1.15 (s, CH₂), 0.83-0.80 (t, CH₃).

Poly(9,9-dioctylfluorene) (PF8) was prepared analogously with pale green powder (0.24 g, yield of 79.27%). GPC: M_n of 4.66 × 10⁴ with the PDI of 1.97. ¹H NMR (400MHz, CDCl₃, 298 K) δ (ppm): 7.86-7.84 (m, ArH), 7.68 (s, ArH), 2.13 (s, CH₂), 1.44 (s, CH₂), 0.84-0.80 (t, CH₃).



Figure S1. ¹H NMR spectra of PF8-*co*-DAF8 and PF8 compounds in CDCl₃.



Figure S2. GPC curves of PF8 and PF8-co-DAF8 compounds.



Figure S3. Cyclic voltammetry of the PF8-*co*-DAF8 compounds for the various fractions of nitrogen heteroatomic substitutions.



Figure S4. ¹H NMR spectrum of PF8 in d8-toluene.



Figure S5. AFM topographic images of PF8-*co*-DAF8 20% film spin-coated from fresh CHCl₃ (a, 5 mg/mL) and toluene (b, 8 mg/mL) solution on Si substrates. Corresponding film thickness are both about 70~80 nm.



Figure S6. EL spectra of PLEDs based on PF8-*co*-DAF8 (50%) gelation films spin-coated from toluene (3 mg/ml, Film thickness is about ~80 nm).



Figure S7. EL spectra of PLEDs based on PF8-*co*-DAF8 (50%) non-gelation films spin-coated from CHCl₃ solution (3 mg/ml. Film thickness is about ~80 nm.).



Figure S8. EL spectra of PLEDs based on PF8 film spin-coated from pristine CHCl₃ solution (5 mg/mL).



Figure S9. Brightness-voltage (B-V) curves of PLEDs based on PF8-*co*-DAF8 (50%) gelation and non-gelation films.



Figure S10. Current efficiency-voltage (C. E.-V) curves of PLEDs based on PF8-*co*-DAF8 (50%) gelation and non-gelation films.

Concentration (mg/ml)	Gel	Gelation time (h)
10	yes	0.2
8	yes	0.5
7	yes	0.8
6	yes	1.2
5	yes	2
4	yes	4
3	yes	6
2	no	-

Tables S1. Gel formation properties of PF8-co-DAF8 (50%) in toluene solution at 298 K.

Table S2. Gel experimental results of PF8-*co*-DAF8 in various solvents with different boiling points, polar points and solubility parameters.^a

Solvent	PF8-co-DAF8	PF8	Toluene	THF	Bromobenzene	DCM	Triethylbenzene	CHCl ₃
Boiling point (°C)	-	-	110	65	156	40	164	61.3
Polarity	> 0	0	0.001	0	0.029	0.12	0	0.20
Solubility parameter (cal/cm ³) ^{1/2}	>9.3	9.3	8.9	9.9	10.0	9.7	9.3	9.3
Gelation ^b	-	-	Y	Ν	Ν	Ν	Y	Ν

^aConcentration: 10 mg/ml, Aged time: 8 h. ^bY = Gelation, N = Solution, P = Precipitation.

Table	S3. Summary	of decay	time of	f PF8-co-DAF	8 (20%)	solution,	gels	and	PF8	gels
(prepa	ared in DCE) at d	lifferent P	L wavele	engths.						
-										
	Sample		Wavelengtl	h (nm) A	τ_{I} ((ps) A	2	τ_2 (p	5)	

Sample	Wavelength (nm)	A_1	τ_{I} (ps)	A_2	τ_2 (ps)
	428	1	386		
PF8-co-DAF8	451	1	402		
Toluene solution	486	1	409		
	427	1	334		
PF8-co-DAF8	445	1	484		
gels	463	1	552		
	492	1	611		
	440	1	164		
	472	1	185		
Frø gels	500	0.94	194	0.06	690
	550	0.78	200	0.22	1034

^aThe excitation wavelength was 390 nm, and the PL emission maxima were monitored in each case. The concentration of PF8-*co*-DAF8 in dilute solutions was 10⁻⁵ mg/ml in toluene.

1 Zhao, J.-F.; Chen, L.; Sun, P.-J.; Hou, X.-Y.; Zhao, X.-H.; Li, W.-J.; Xie, L.-H.; Qian, Y.; Shi, N.-E.; Lai, W.-Y.; Fan, Q.-L.; Huang, W., *Tetrahedron* 2011,**67**, 1977. 2 Li, W.-J.; Liu, B.; Qian, Y.; Xie, L.-H.; Wang, J.; Li, S.-B.; Huang, W. *Polym. Chem.* 2013, **4**, 1796.