Supporting Information

Suppressing the Non-radiative Energy Loss in Non-fullerene-based Organic Solar Cells *Via* Solid Additives of Racemic and Isotactic Nitroxide Radical Polymonothiocarbonates

Yuyan Tao,[†a] Xuanyu Zhou,[†a] Xiao Zheng,[a] Huiyuan Peng,[a] Min Gyu Kang,[c] Pengzhi Guo,[a] Xunchang Wang,[b] Renqiang Yang,[b] Ergang Wang,[d] Hanyoung Woo[c] and Yangjun Xia*[a]

[a] *Organic Semiconductor Materials and Applied Technology Research Centre of Gansu Province, School of Materials Science and Engineering, Lanzhou Jiaotong University, Lanzhou, 730070, P. R. China.*

[b] *Key Laboratory of Optoelectronic Chemical Materials and Devices (Ministry of Education), School of Optoelectronic Materials and Technology, Jianghan University, Wuhan, 430056, P. R. China.*

[c] *Department of Chemistry, KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 02841, Republic of Korea.*

[d] *Department of Chemistry and Chemical Engineering, Chalmers University of Technology, SE-41296 Göteborg, Sweden.*

*Corresponding authors:

E-mail addresses: xiayangjun2015@126.com

1. Experiment Section

1.1 Materials

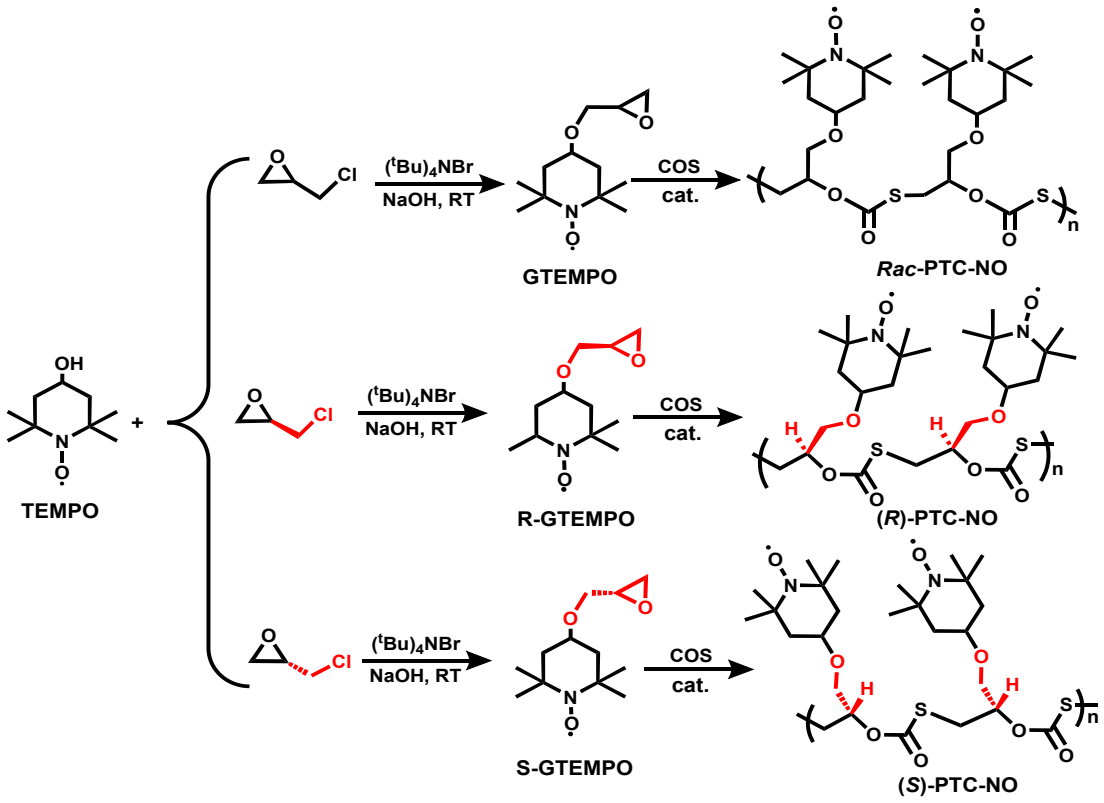
Racemic and isotactic 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (GTEMPO), (*R*)-4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl ((*R*)-GTEMPO), (*S*)-4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl ((*S*)-GTEMPO) were synthesised following an optimised procedure according to the literature. [(*R*,*R*)-N,N'-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine]chromium (III) chloride was purchased from Shanghai Haohong Scientific Co., Ltd. Bis(triphenylphosphine)iminium chloride (PPNCl) was obtained from Anhui Senrise Technologies Co., Ltd. Other reagents and solvents were purchased from commercial sources and used as received, with the exception of toluene and dichloromethane, which were freshly distilled immediately prior to use. PDINN was purchased from Solarmer Materials (Beijing) Inc. (China). PM6 and Y6 were obtained from Hyper PV Technology. Co., Ltd.

1.2 General characterization

^{1}H NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500 MHZ. Film absorption spectra were obtained by using a UV-visible spectrophotometer (HITACHI, Japan). Analytical gel permeation chromatography (GPC) measurements (Waters GPC 2410) were performed in tetrahydrofuran (THF) relative to polystyrene standards. Electron paramagnetic resonance (EPR) measurements were taken using a Bruker A300-9 5/12 apparatus. The test parameters and results of optical rotation are obtained by polarimeter (WZZ-2B). Cyclic voltammetry (CV) analysis was performed on a CHI 600D electrochemical workstation (Shanghai Chenhua Co.) at a scan rate of 50 $mV \cdot s^{-1}$. Atomic force microscopy (AFM) measurements (Agilent 5400) were performed with tapping mode. Transmission electron microscopy (TEM) images were acquired with a Tecnai G2 F20 (FEI, Hillsboro, OR, USA) transmission electron microscope at an

accelerating voltage of 200 kV. Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements at the 9A U-SAXS beamline of the Pohang Accelerator Laboratory (PAL), Republic of Korea, with a beam energy of 11.07 KeV and incident angles of 0.12°. Electroluminescence (EL), quantum efficiency (EQE_{EL}) and the highly sensitive EQE measurements were performed by applying external voltage/current sources through the devices (lightSky Tech., LST-QE).

1.3 Synthesis of the monomers and nitroxide radical polymers



Scheme S1. Synthetic route of the monomers and PTC-NOs of *Rac*-PTC-NO, (*R*)-PTC-NO and (*S*)-PTC-NO

Synthesis of the GTEMPO:

A mixture of racemic epichlorohydrin (5 mL, 60 mmol) and $(^tBu)_4NBr$ (0.75 g, 2.3 mmol) in an aqueous NaOH solution (8 mL, 50%) was stirred for 10 min at room temperature in a three-necked flask. Then, a solution of TEMPO (6.18 g, 35.88 mmol) in THF (50 mL) was added dropwise. The

reaction mixture was stirred vigorously overnight at room temperature and then poured into ice water. The product was extracted with ethyl acetate (three times), and the combined organic layers were washed with deionised water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (hexanes/ethyl acetate, 8:1 v/v). The collected mixture containing the product were concentrated and recrystallised from hexane to yield 5.8 g of dark red needle-like crystals, representing a 71% yield based on TEMPO. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.37 (s, 1H), 3.69 (dd, 1H), 3.61 (m, 1H), 3.36 (dd, 1H), 3.08 (m, 1H), 2.74 (pseudo-t, 1H,), 2.54 (dd,1H), 1.86 (dd, 2H), 1.4 (pseudo-t), 1.15 (d, 12H).

(*R*)-GTEMPO: The synthesis method is the same as that of GTEMPO. Just replace racemic epichlorohydrin with left-handed epichlorohydrin. (Yield: 71%).^{1}H NMR (500 MHz, $CDCl_3$): δ 5.37 (s, 1H), 3.69 (dd, 1H), 3.61 (m, 1H), 3.36 (dd, 1H), 3.08 (m, 1H), 2.74 (pseudo-t, 1H), 2.54 (dd,1H), 1.86 (dd, 2H), 1.4 (pseudo-t), 1.15 (d, 12H).

(*S*)-GTEMPO: The synthesis method is the same as that of GTEMPO. Just replace racemic epichlorohydrin with dextrorotatory epichlorohydrin. (Yield: 70%).^{1}H NMR (500 MHz, $CDCl_3$): δ 5.37 (s, 1H), 3.69 (dd, 1H), 3.61 (m, 1H), 3.36 (dd, 1H), 3.08 (m, 1H), 2.74 (pseudo-t, 1H), 2.54 (dd,1H), 1.86 (dd, 2H), 1.4 (pseudo-t), 1.15 (d, 12H).

Synthesis of the *Rac*-PTC-NO:

The [(R,R)-N,N'-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine]chromium(III)(40mg, 0.068mmol), PPNCl (39mg, 0.068mmol), GTEMPO (3.88g, 17mmol) and 10ml mixture solvent (DCM: Toluene, 1:1 v/v) were added to 200 ml stainless steel reactor vessel, This corresponds to a catalyst/co-catalyst/GTEMPO molar ratio of 1/1/250. The reactor was pressurised with COS to 1.0 MPa, and the reaction was allowed to proceed for 24 h. After depressurisation, the crude

product was obtained by removing the solvent under reduced pressure. Then the coarse polymers were purified by silica gel column chromatography using toluene as eluent. The solution of the polymer in toluene was condensed to 15 mL and then poured into hexane (200 mL). The precipitate was collected and dried under vacuum overnight. (yield: 74%). Mn = 5425 g/mol, PDI = 1.7.

(*R*)-PTC-NO: The synthesis method is the same as that of *Rac*-PTC-NO. Just replace (*R*)-GTMPO with GTEMPO. (yield: 76%). M_n = 3031 g/mol, PDI = 1.5.

(*S*)-PTC-NO: The synthesis method is the same as that of *Rac*-PTC-NO. Just replace (*S*)-GTMPO with GTEMPO. (yield:77%). M_n = 3562 g/mol, PDI = 1.6.

2. Fabrication and characterization of the NFAs-OSCs

At the beginning, the patterned indium tin oxide (ITO) coated glass substrates were cleaned and treated in a UV-Ozone Cleaner for 10 min. PEDOT:PSS (30 nm) was spin-casted on it, and heated at 160 °C for 15 min. Then, the active layer materials (PM6:Y6, 1:1.2 wt. ratio) in chloroform with and without 0.5wt.% PTC-NOs additives in relative to PM6 weight were spin-coated on the PEDOT:PSS alongside the utilisation of 0.5% 1-chloronaphthalene (CN) (V_{CN} : V chloroform, 0.5:100) as solvent additive. After that, the PDINN was deposited on top of the active layer by spin-coating, and then silver was evaporated with a shadow mask as the cathode (100 nm) under vacuum (5×10^{-4} Pa). The current density-voltage (*J-V*) characteristics of the devices were measured in a glovebox with a Keithley 2400 Source meter under 1 sun, AM 1.5G spectra (100 $mW\cdot cm^{-2}$) from a solar simulator (XES-70S1, San-EI Electric Co). The EQE was measured with a commercial EQE/incident photon to charge carrier efficiency (IPCE) setup (7-SCSpecIII, Beijing 7-star Opt. In. Co.), in which an integrated standard single-crystal Si photovoltaic cell (S1337-101BQ, SOFN instruments co., Ltd. calibrated by National Institute of Metrology of China) was employed to calibrate the light intensity at each wavelength.

3. Measurements of the photo/thermal stability of the NFAs-OSCs

The photo/thermal stability of the OSCs from PM6:Y6-based NFAs-OSCs with and without 0.5wt.%

PTC-NOs additives were investigated under a controlled atmosphere in a nitrogen glovebox (Etelux Co.) containing less than 1 ppm oxygen and moisture. The photostability of the PM6:Y6-based OSCs with and without 0.5wt.% PTC-NOs additives was evaluated under 1-sun white light LED irradiation inside a glovebox containing less than 1 ppm of oxygen and water. The *J-V* characteristics and PCEs of the OSCs were measured at times of 120 h under continuous light illumination. For thermal stability assessment, the devices were annealed at 60 °C in the same glovebox environment. Their performance parameters (*J-V* and PCEs) were similarly tracked over storage times of 100 h.

4. Measurements of the charge mobility of the PM6:Y6 blend films

The hole and electron mobility (μ_h and μ_e) were measured using the space charge limited current (SCLC) method, μ_h and μ_e employing a device architecture of ITO/PEDOT:PSS/blend film/MoO_3/Ag for hole-only devices and ITO/ZnO/blend film/PFN/Ag for electron-only devices, The μ_h and μ_e were calculated using Equation.

$$\mu_{h/e} = \frac{8d^3J}{V^2 9\varepsilon_r\varepsilon_0}$$

Where ε_0 is the permittivity of the free space, ε_r is the relative dielectric constant of the transport medium and is estimated to be 3, *V* is the internal potential, *J* is the current density in the devices, and *d* is the thickness of the blend films.

5. Supplementary Figures and Tables

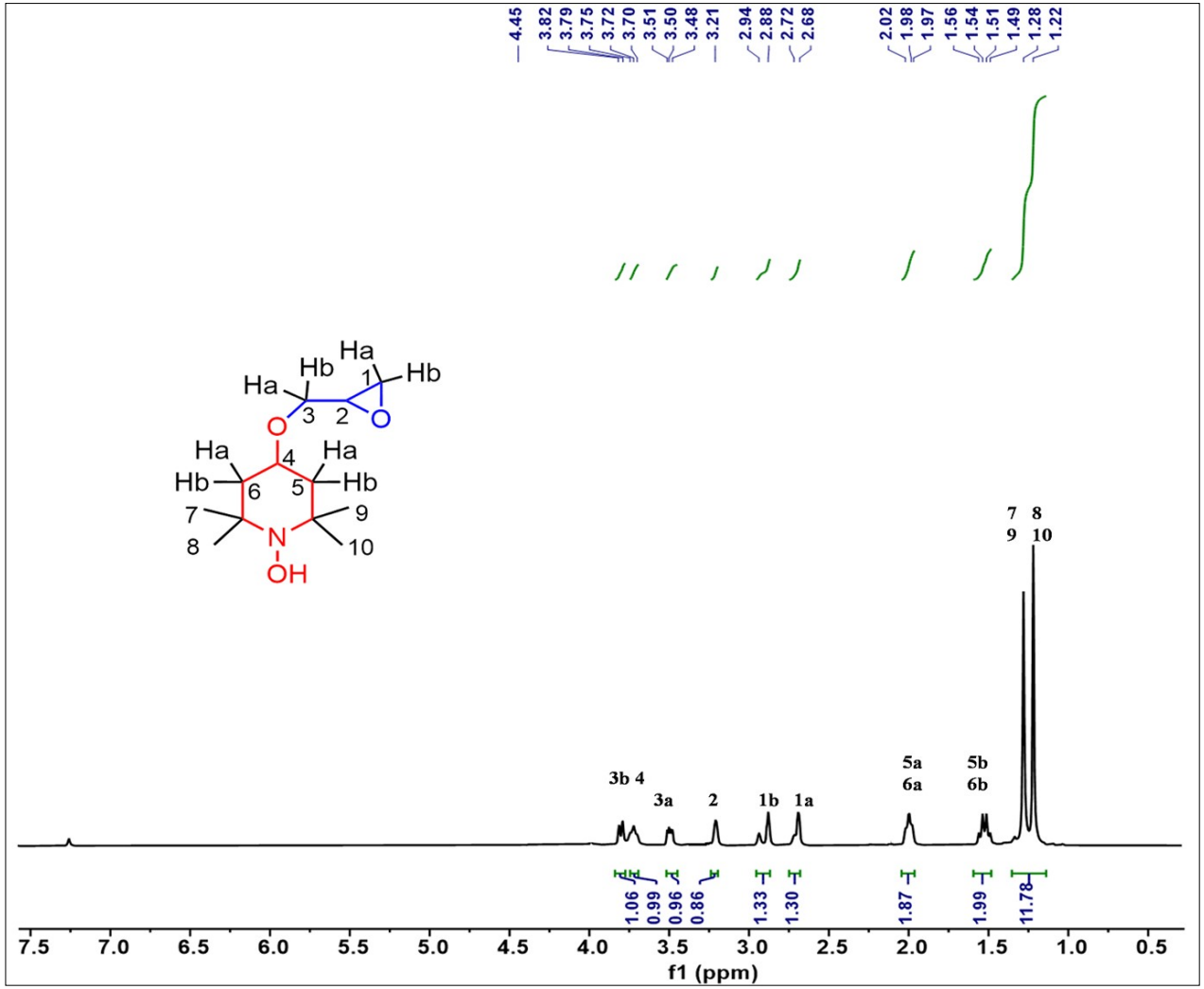


Fig. S1 ^{1}H NMR spectrum of GTEMPO after reduction with erythorbic acid in $DCCl_3$

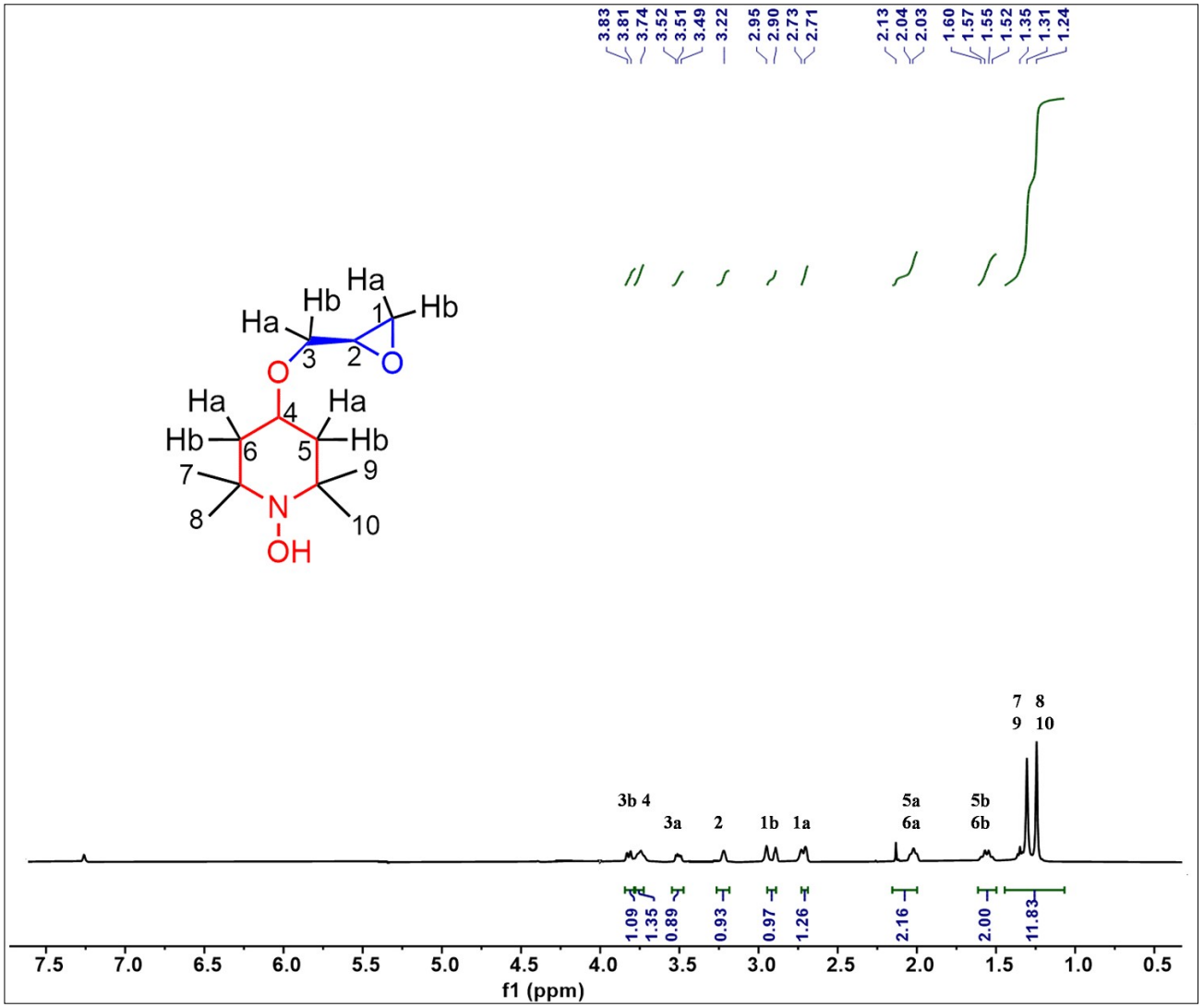


Fig. S2 ^{1}H NMR spectrum of (*R*)-GTEMPO after reduction with erythorbic acid in $DCCl_3$

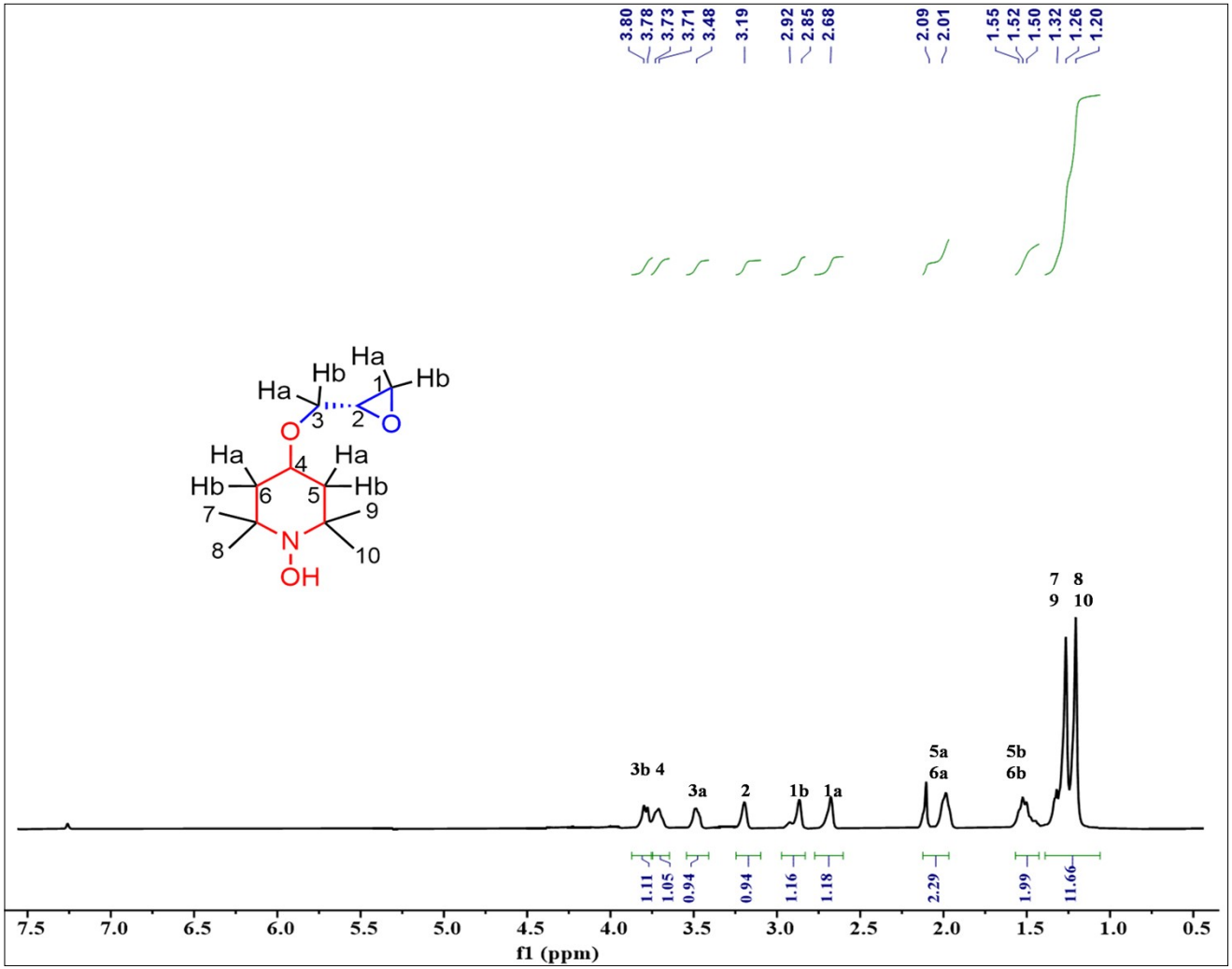


Fig. S3 ^{1}H NMR spectrum of (*S*)-GTEMPO after reduction with erythorbic acid in $DCCl_3$

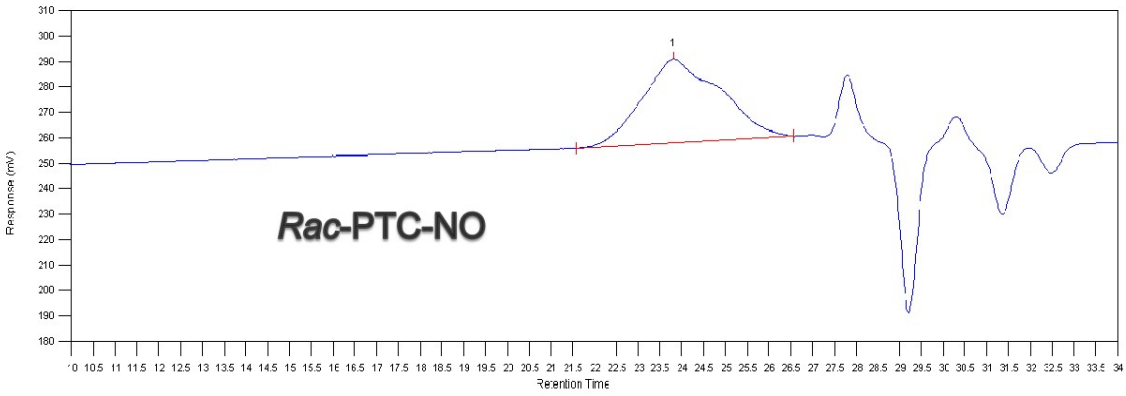


Fig. S4 Gel Permeation Chromatography (GPC) curve of *Rac*-PTC-NO.

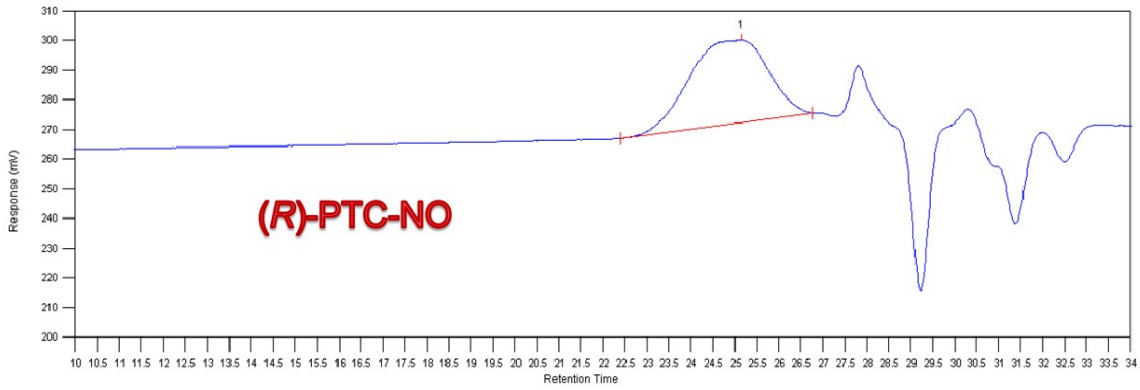


Fig. S5 Gel Permeation Chromatography (GPC) curve of (*R*)-PTC-NO.

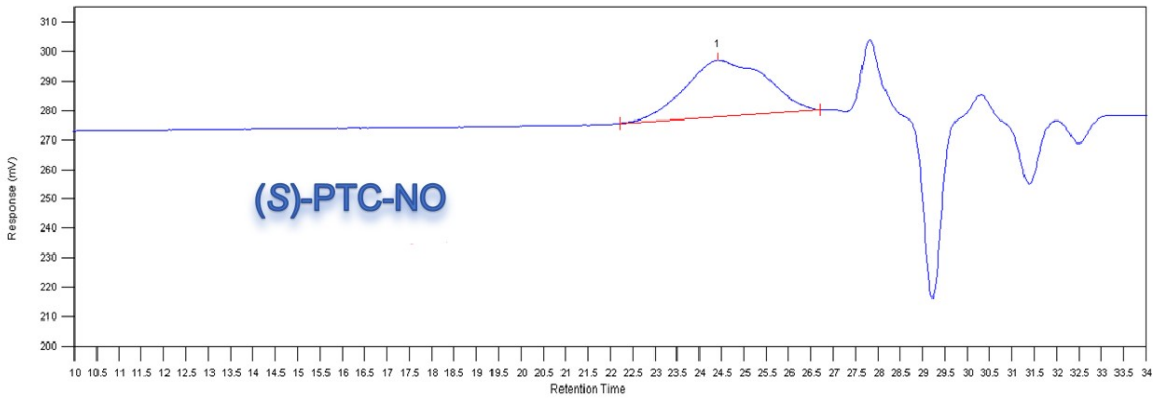


Fig. S6 Gel Permeation Chromatography (GPC) curve of (*S*)-PTC-NO.

Table S1 Optical rotation test parameters of *Rac*-PTC-NO, (*R*)-PTC-NO and (*S*)-PTC-NO

Polymer	Light source(nm)	*L*(nm)	T(°C)	solvent	C(mg/mL)	α(°C)
Rac-PTC-NO	589.3	10	26.6	DCM	10	0
(*R*)-PTC-NO	589.3	10	26.6	DCM	10	-21
(*S*)-PTC-NO	589.3	10	26.6	DCM	10	+21

Table S2 Photovoltaic parameters of the PM6:Y6-based NFAs-OSCs with different contents addition of *Rac*-PTC-NO additives

Active Layer	Additive	*Jsc* (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
PM6:Y6	Without	25.45	0.839	73.68	15.73
	0.3 wt.% *Rac*-PTC-NO	24.68	0.838	78.74	16.28
	0.5 wt.% *Rac*-PTC-NO	25.15	0.853	77.34	16.59
	1.0 wt.% *Rac*-PTC-NO	24.82	0.843	75.83	15.86
	2.0 wt.% *Rac*-PTC-NO	25.45	0.835	74.03	15.73
	5.0 wt.% *Rac*-PTC-NO	24.21	0.844	73.24	14.97

Table S3 Photovoltaic parameters of the PM6:Y6-based NFAs-OSCs with different contents addition of (*R*)-PTC-NO additives

Active Layer	Additive	*Jsc* (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
PM6:Y6	Without	25.45	0.839	73.68	15.73
	0.3 wt.% (*R*)-PTC-NO	25.59	0.848	75.91	16.47
	0.5 wt.% (*R*)-PTC-NO	26.85	0.852	75.63	17.30
	1.0 wt.% (*R*)-PTC-NO	25.54	0.853	74.75	16.28
	2.0 wt.% (*R*)-PTC-NO	25.27	0.845	74.34	15.87
	5.0 wt.% (*R*)-PTC-NO	24.43	0.837	74.13	15.16

Table S4 Photovoltaic parameters of the PM6:Y6-based NFAs-OSCs with different contents

Active Layer	Additive	*Jsc* (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
PM6:Y6	Without	25.45	0.839	73.68	15.73
	0.3 wt.% (*S*)-PTC-NO	25.80	0.845	75.12	16.38
	0.5 wt.% (*S*)-PTC-NO	26.82	0.855	75.89	17.40
	1.0 wt.% (*S*)-PTC-NO	25.70	0.843	75.21	16.29
	2.0 wt.% (*S*)-PTC-NO	24.85	0.846	73.42	15.44
	5.0 wt.% (*S*)-PTC-NO	23.57	0.837	73.93	14.58

addition of (*S*)-PTC-NO additives

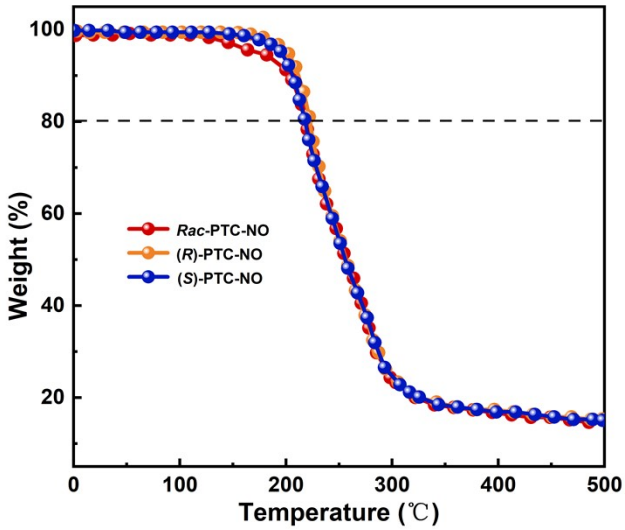


Fig. S7 Thermogravimetric (TG) curves of *Rac*-PTC-NO, (*R*)-PTC-NO and (*S*)-PTC-NO.

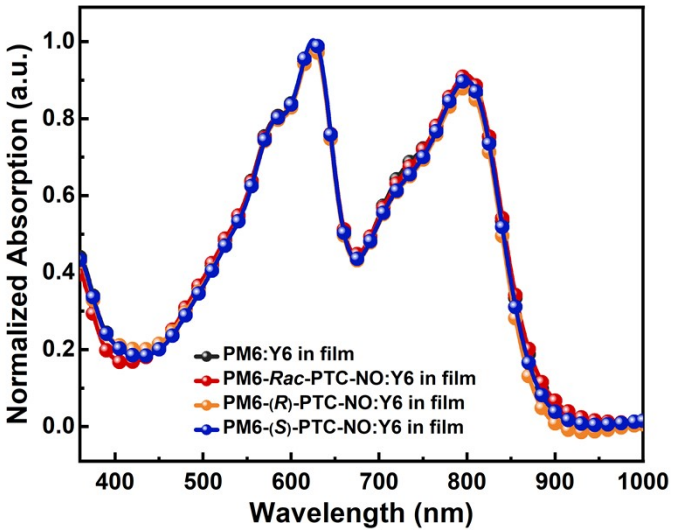


Fig. S8 UV-vis absorption spectra of PM6: Y6 blend films with and without 0.5 wt.% *Rac*-PTC-NO, (*R*)-PTC-NO and (*S*)-PTC-NO.

Table S5 The structural parameters of the original and optimal blend membranes with and without 0.5 wt.% *Rac*-PTC-NO, (*R*)-PTC-NO and (*S*)-PTC-NO radical additives were measured by GIWAXS.

Active layer	additive	(010) Diffraction peak				(100) Dfraction peak			
		q_z [Å^{-1}]	d-spacing [Å^{-1}]	FWHM [Å^{-1}]	CCl [Å]	q_z [Å^{-1}]	d-spacing [Å^{-1}]	FWHM [Å^{-1}]	CCl [Å]
PM6/Y6	without	1.704	3.687	0.186	30.065	0.286	21.969	0.0608	91.974
	Rac-PTC-NO	1.709	3.677	0.177	31.593	0.288	21.817	0.0581	96.247
	(*R*)-PTC-NO	1.716	3.662	0.172	32.512	0.294	21.371	0.0576	97.084
	(S)-PTC-NO	1.714	3.666	0.175	31.954	0.292	21.666	0.0578	96.748

Table S6. Hole and electron mobility of PM6:Y6 blend films with and without 0.5 wt.% *Rac*-PTC-NO, (*R*)-PTC-NO and (*S*)-PTC-NO additives

Active layer	Additives	Thickness (nm)	μ_h ($cm^2v^{-1}s^{-1}$)	μ_e ($cm^2v^{-1}s^{-1}$)	μ_h/μ_e
PM6:Y6	Without	100	4.03×10^{-4}	2.22×10^{-4}	1.82
	Rac-PTC-NO	100	5.45×10^{-4}	3.08×10^{-4}	1.78
	(*R*)-PTC-NO	100	5.52×10^{-4}	4.17×10^{-4}	1.32
	(*S*)-PTC-NO	100	5.75×10^{-4}	3.98×10^{-4}	1.44