Supporting information

The Role of Hydrogen-Bond Between Piperazine and Fullerene Molecules in Stabilizing Polymer:Fullerene Solar Cell Performance

Zerui Li,[1,2] Jiankai Shan,[3] Lingpeng Yan,[2,4] Huimin Gu,[2,5] Yi Lin,[6] Hongwei Tan,[3,*] Chang-Qi Ma,[1,2 *]

1. School of Nano-Tech and Nano-Bionics, University of Science and Technology of China, 398 Jinzhai Road, Hefei, 230026, P. R. China.
2. Printable Electronics Research Center, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Ruoshui Road 398, SEID, SIP, 215123, P. R. China
3. College of Chemistry, Beijing Normal University, Beijing, 19 Waida Street, Xinjie Kou, Beijing, 100875, P. R. China
4. Institute of New Carbon Materials, Taiyuan University of Technology, 79 Yingze Street, Taiyuan 030024, P. R. China.
5. Key Laboratory of Interface Science and Engineering in Advanced Materials, Ministry of Education, Taiyuan University of Technology, 79 Yingze Street, Taiyuan 030024, P. R. China.
6. Department of Chemistry, Xi'an Jiaotong Liverpool University, Renai Road 11, SEDI, SIP, Suzhou, 215123, P. R. China

*Corresponding Author: hongwei.tan@bnu.edu.cn; cqma2011@sinano.ac.cn

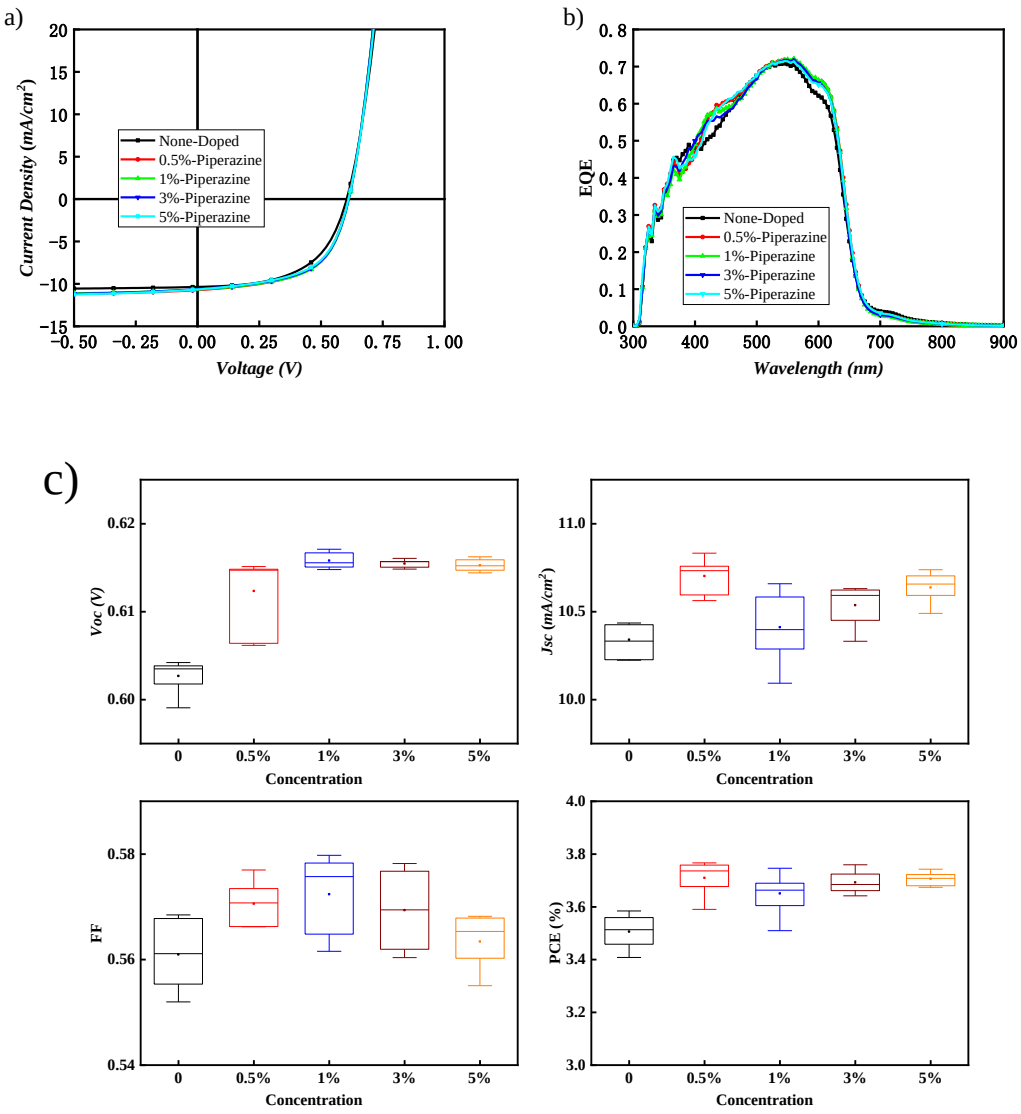


Figure S1. a) *J-V* curves, b) EQE spectra and c) statistical data of polymer solar cell based on P3HT:$PC_{61}BM$ doped with piperazine

Table S1. Performance of polymer solar cell based on P3HT:$PC_{61}BM$ doped with piperazine

D.C.	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
0	0.60	10.34±0.09	0.56±0.01	3.48±0.09
0.5%	0.61	10.70±0.10	0.57±0.00	3.71±0.06
1%	0.62	10.41±0.19	0.57±0.01	3.67±0.09
3%	0.62	10.56±0.13	0.57±0.01	3.69±0.04
5%	0.62	10.64±0.08	0.56±0.00	3.69±0.05

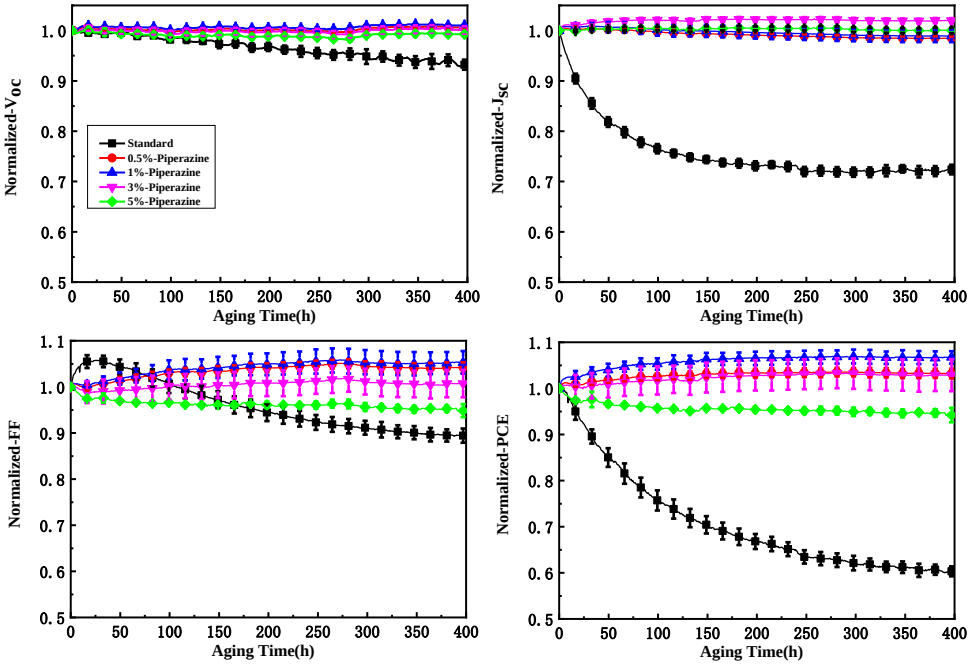


Figure S2. Degradation curves of polymer solar cell based on P3HT:$PC_{61}BM$ doped with piperazine

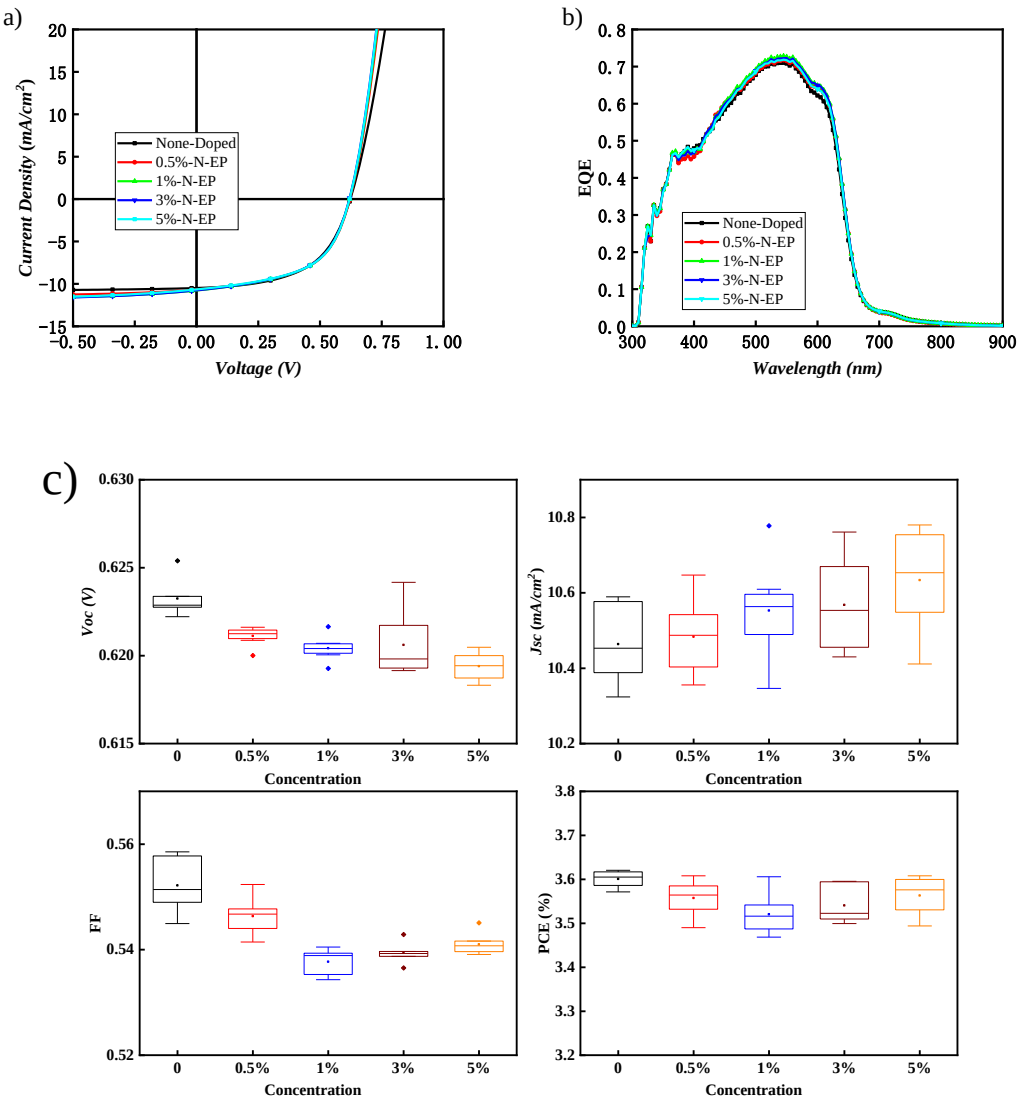


Figure S3. a) *J-V* curves, b) EQE spectra and c) statistical data of polymer solar cell based on P3HT:$PC_{61}BM$ doped with N-EP

Table S2. Performance of polymer solar cell based on P3HT:$PC_{61}BM$ doped with N-EP

D.C.	V_{OC} (V)	J_{SC} (mA/cm²)	FF	PCE (%)
0	0.62	10.46±0.11	0.55±0.01	3.60±0.02
0.5%	0.62	10.48±0.10	0.55±0.00	3.56±0.03
1%	0.62	10.55±0.13	0.54±0.00	3.52±0.04
3%	0.62	10.57±0.12	0.54±0.01	3.56±0.07
5%	0.62	10.63±0.13	0.54±0.00	3.56±0.04

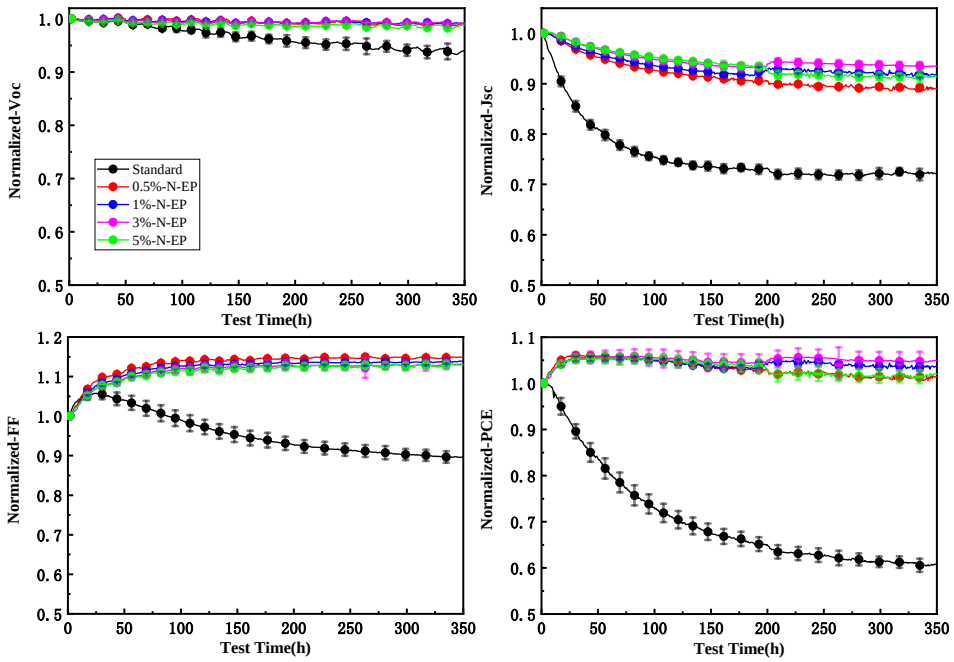


Figure S4. Degradation curves of polymer solar cell based on P3HT:$PC_{61}BM$ doped with N-EP

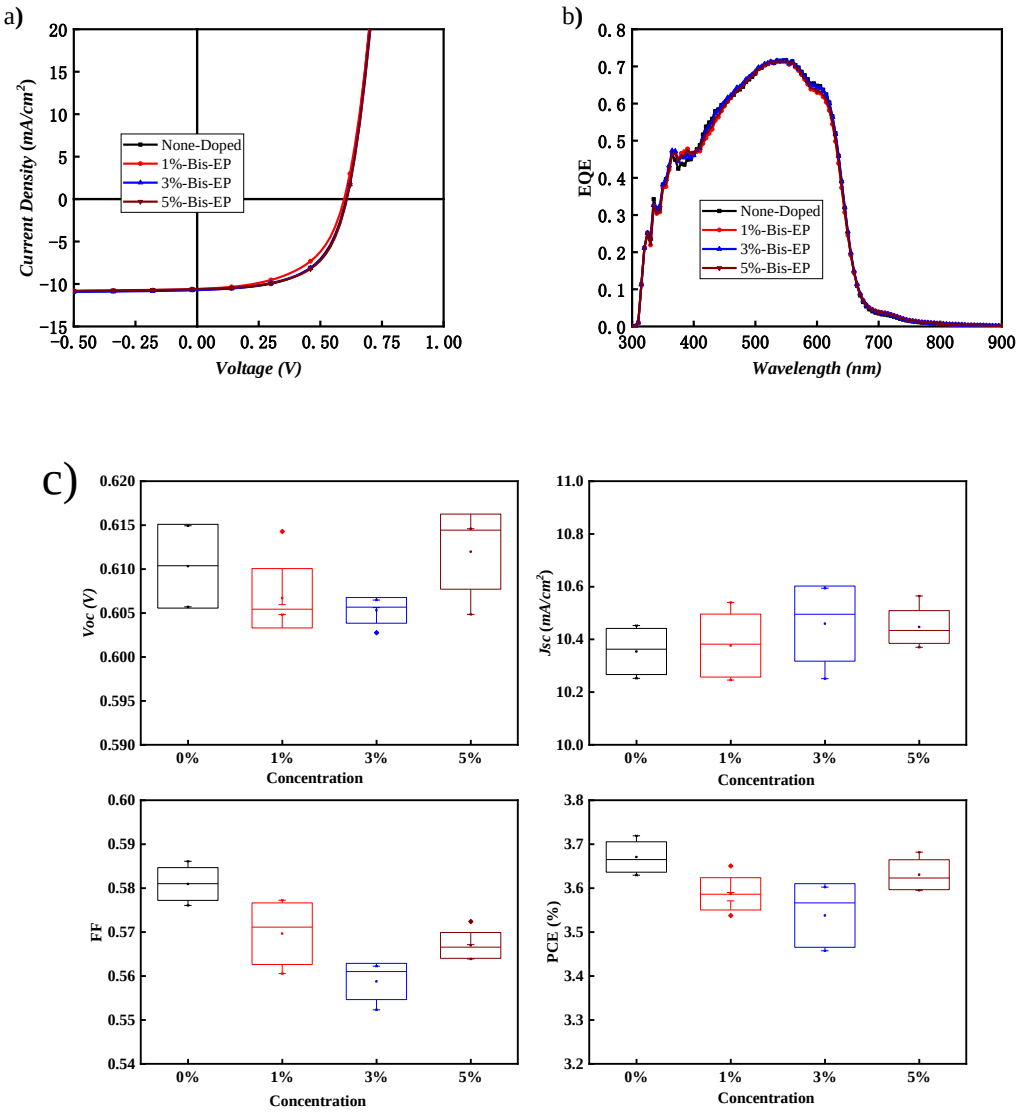


Figure S5. a) *J-V* curves, b) EQE spectra and c) statistical data of polymer solar cell based on P3HT:$PC_{61}BM$ doped with Bis-EP

Table S3. Performance of polymer solar cell based on P3HT:$PC_{61}BM$ doped with Bis-EP

D.C.	V_{OC} (V)	J_{SC} (mA/cm²)	FF	PCE (%)
0	0.61	10.35±0.09	0.58±0.00	3.67±0.04
1%	0.61	10.38±0.12	0.57±0.01	3.59±0.03
3%	0.61	10.46±0.14	0.56±0.00	3.54±0.07
5%	0.61	10.45±0.06	0.57±0.00	3.63±0.03

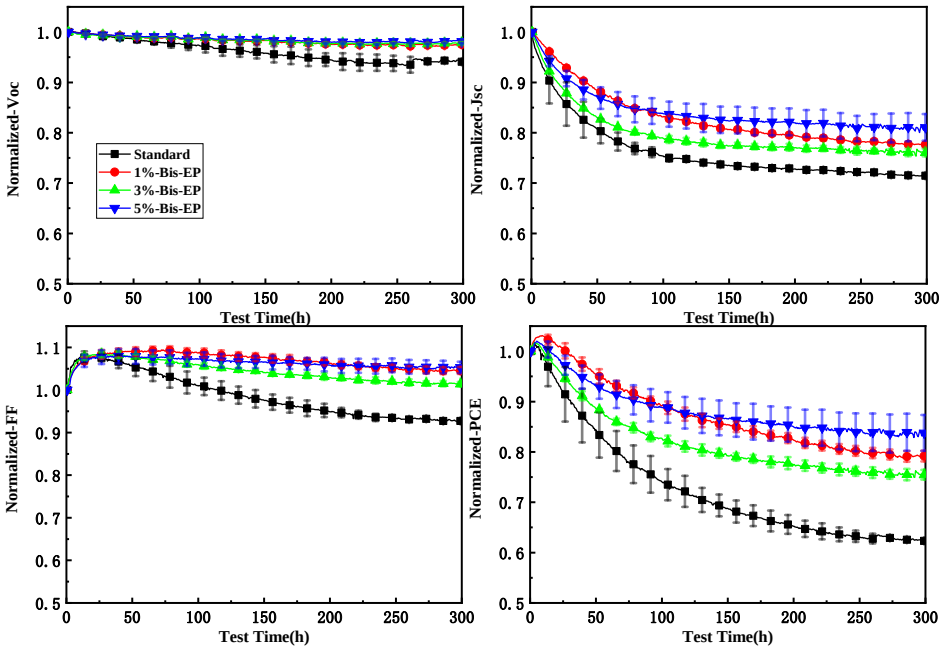


Figure S6. Degradation curves of polymer solar cell based on P3HT:$PC_{61}BM$ doped with Bis-EP

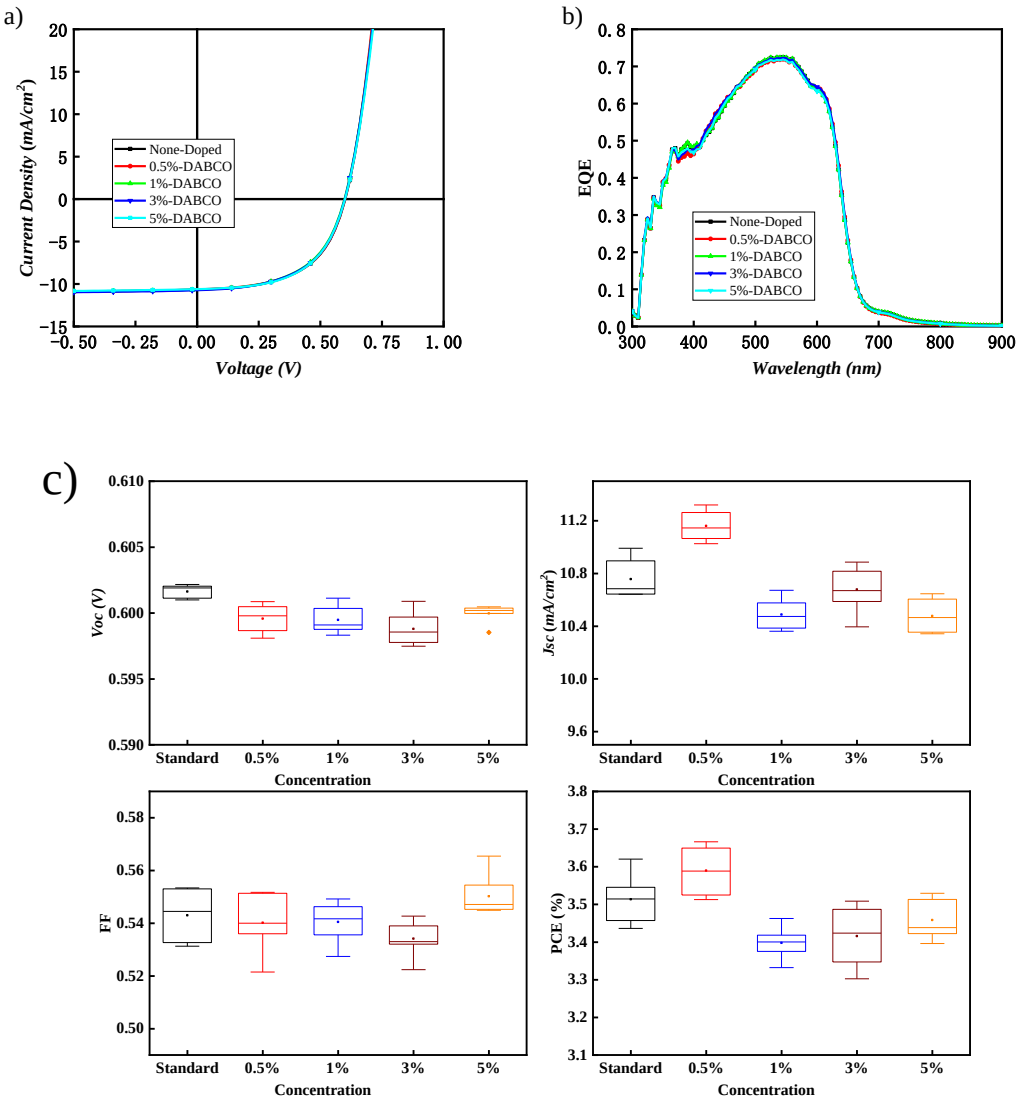


Figure S7. a) *J-V* curves, b) EQE spectra and c) statistical data of polymer solar cell based on P3HT:$PC_{61}BM$ doped with DABCO

Table S4. Performance of polymer solar cell based on P3HT:$PC_{61}BM$ doped with DABCO

D.C.	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
0	0.60	10.71±0.13	0.55±0.00	3.55±0.06
0.5%	0.60	11.09±0.22	0.54±0.01	3.59±0.06
1%	0.60	10.49±0.11	0.54±0.01	3.40±0.04
3%	0.60	10.68±0.16	0.53±0.01	3.42±0.08
5%	0.60	10.48±0.12	0.55±0.01	3.46±0.05

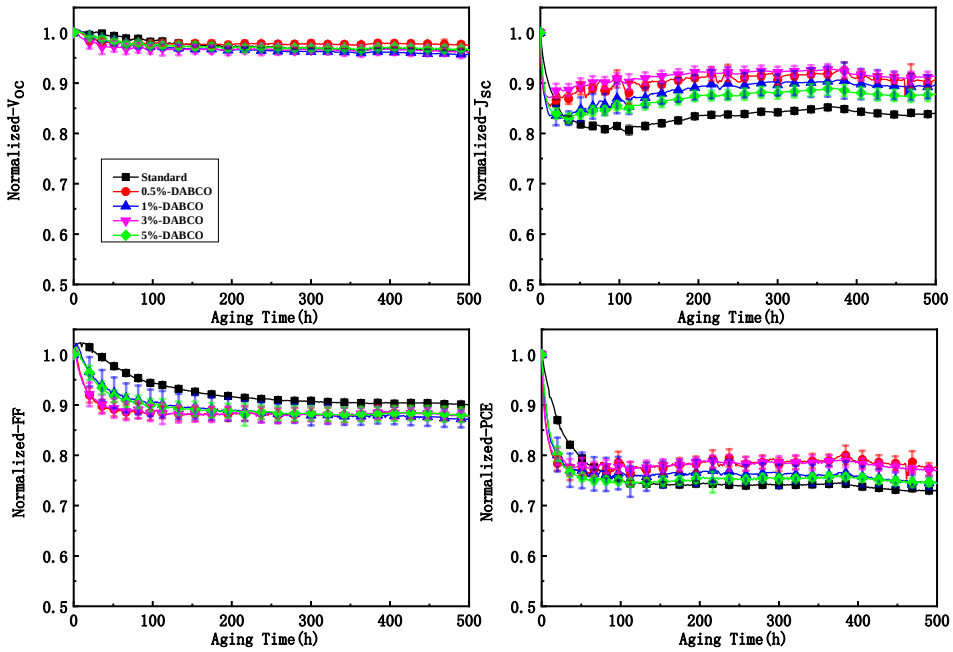


Figure S8. Degradation curves of polymer solar cell based on P3HT:$PC_{61}BM$ doped with DABCO

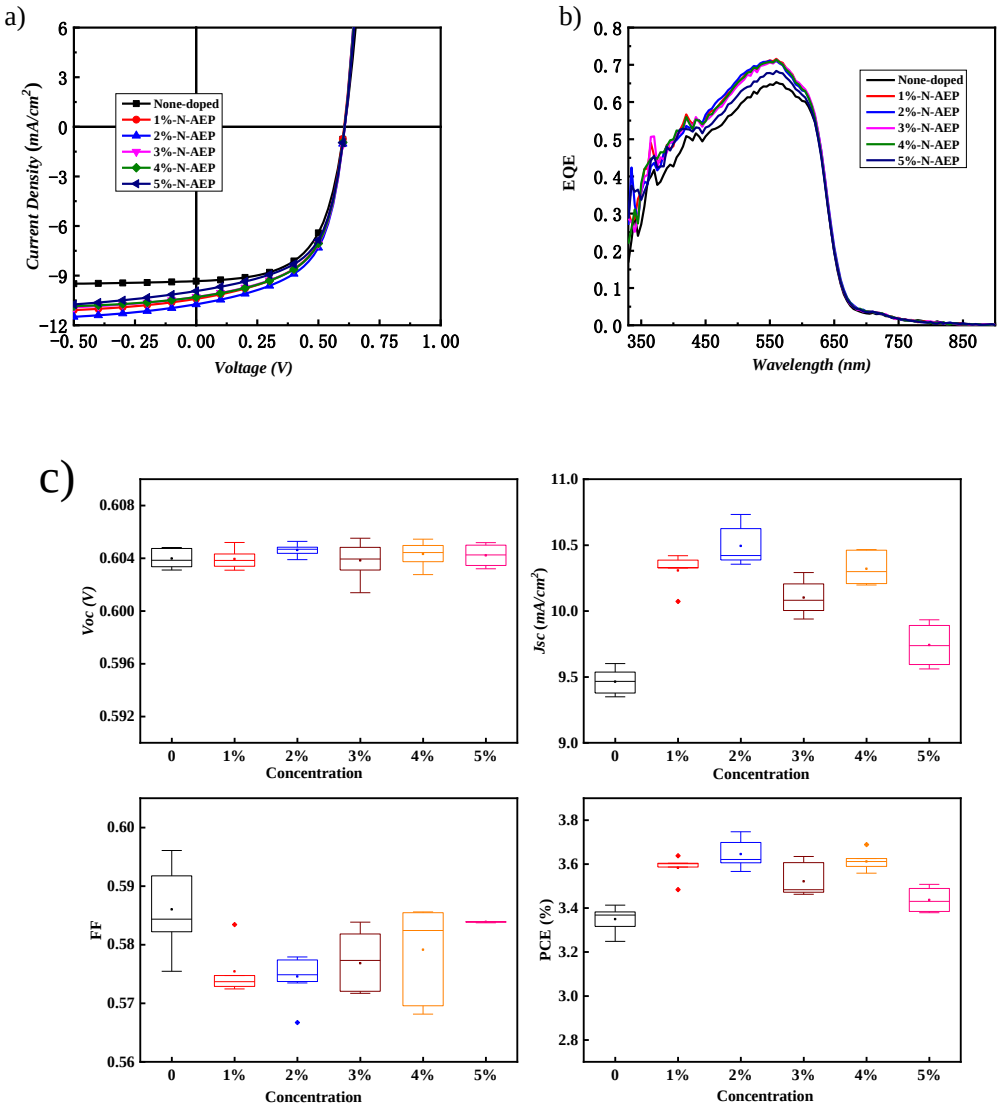


Figure S9. a) *J-V* curves, b) EQE spectra and c) statistical data of polymer solar cell based on P3HT:$PC_{61}BM$ doped with N-AEP

Table S5. Performance of polymer solar cell based on P3HT:$PC_{61}BM$ doped with N-AEP

D.C.	V_{OC} (V)	J_{SC} (mA/cm²)	FF	PCE (%)
0	0.60	9.46±0.10	0.59±0.01	3.35±0.05
1%	0.60	10.28±0.14	0.58±0.01	3.55±0.09
2%	0.60	10.50±0.15	0.58±0.00	3.65±0.06
3%	0.60	10.10±0.13	0.58±0.01	3.51±0.08
4%	0.60	10.33±0.11	0.58±0.01	3.62±0.04
5%	0.60	9.74±0.18	0.58±0.00	3.44±0.63

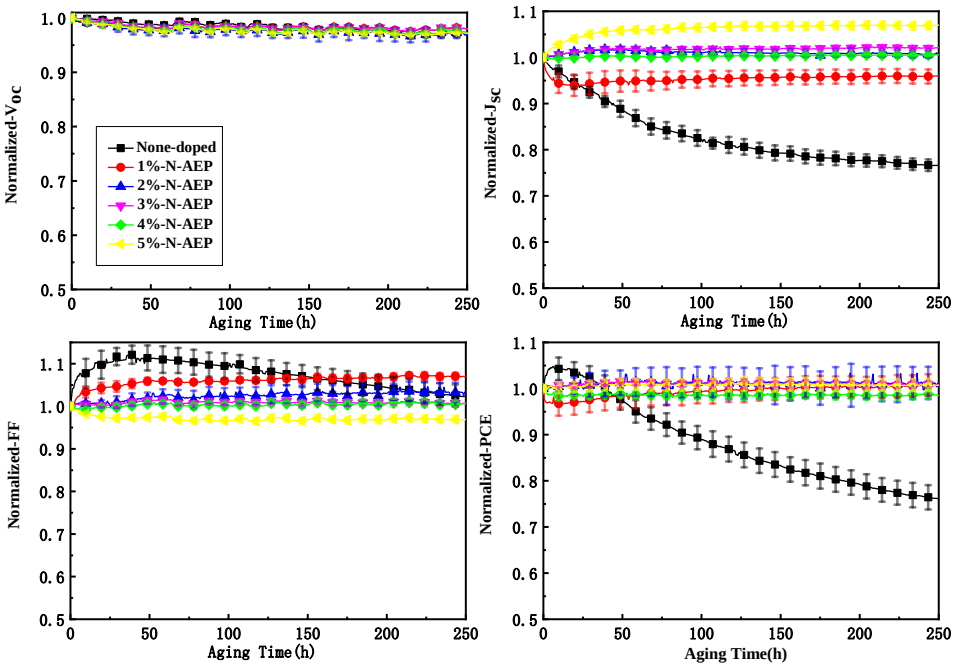


Figure S10. Degradation curves of polymer solar cell based on P3HT:$PC_{61}BM$ doped with N-AEP

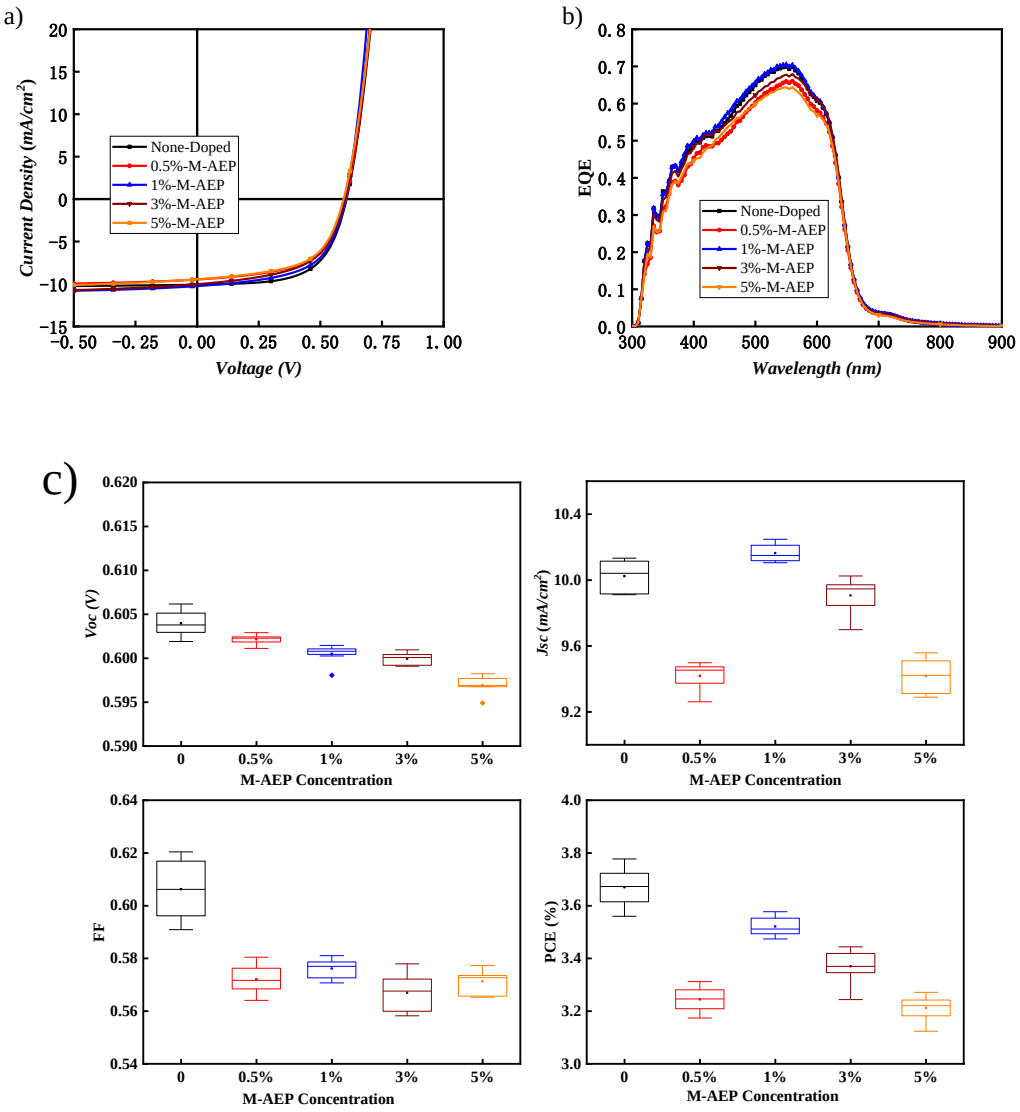


Figure S11. a) *J-V* curves, b) EQE spectra and c) statistical data of polymer solar cell based on P3HT:$PC_{61}BM$ doped with M-AEP

Table S6. Performance of polymer solar cell based on P3HT:$PC_{61}BM$ doped with M-AEP

D.C.	V_{OC} (V)	J_{SC} (mA/cm²)	FF	PCE (%)
0	0.60	10.02±0.10	0.61±0.01	3.67±0.07
0.5%	0.60	9.42±0.09	0.57±0.01	3.25±0.05
1%	0.60	10.16±0.06	0.57±0.01	3.50±0.07
3%	0.60	9.91±0.11	0.57±0.01	3.37±0.06
5%	0.60	9.42±0.10	0.57±0.00	3.21±0.05

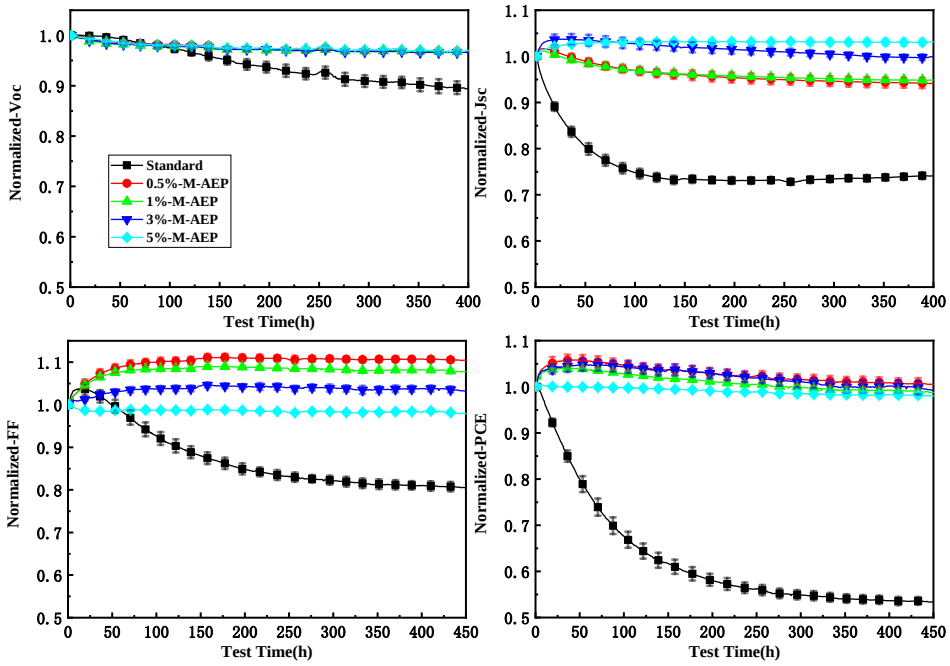


Figure S12. Degradation curves of polymer solar cell based on P3HT:$PC_{61}BM$ doped with M-AEP

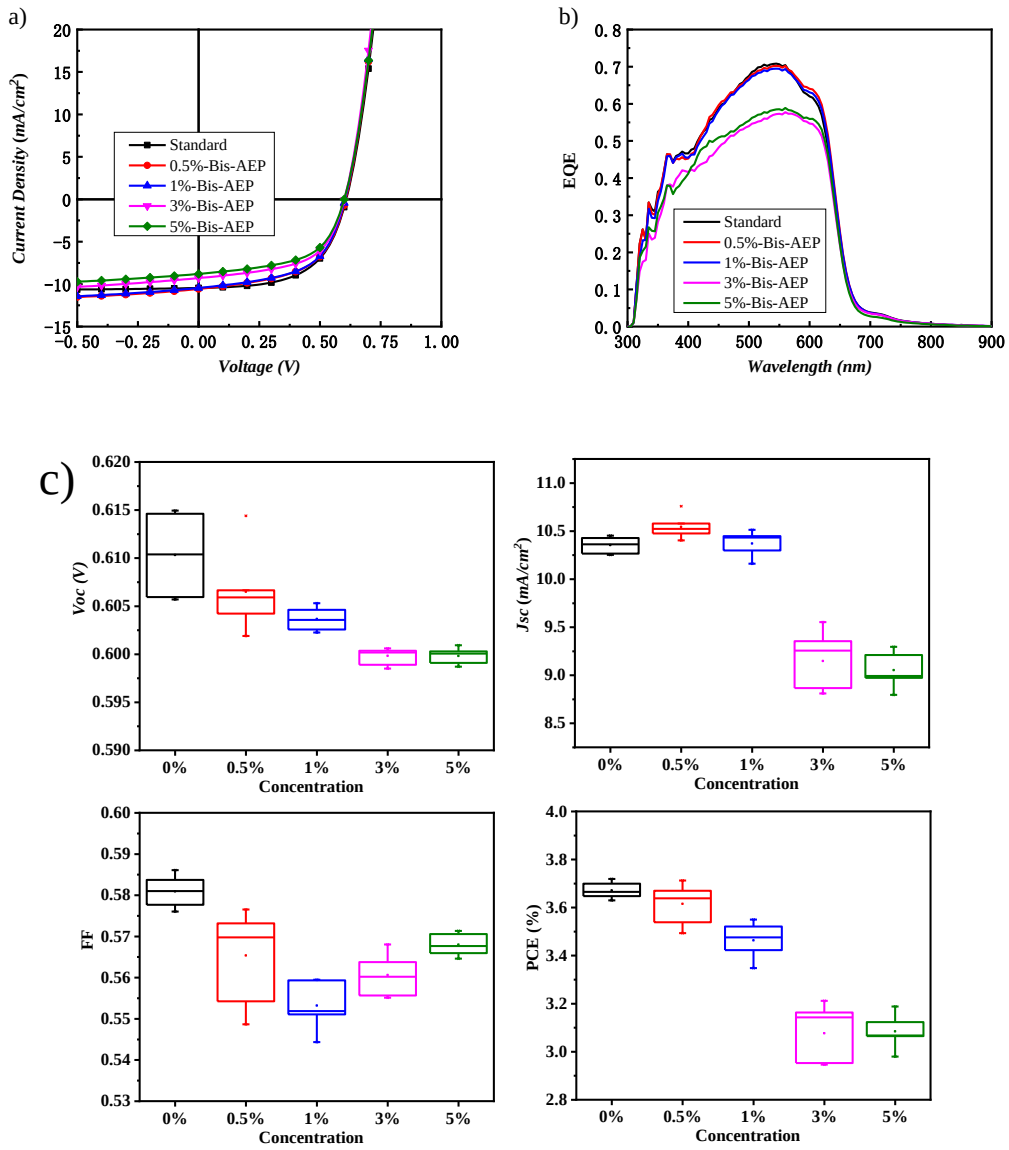


Figure S13. a) *J-V* curves, b) EQE spectra and c) statistical data of polymer solar cell based on P3HT:$PC_{61}BM$ doped with Bis-AEP

Table S7. Performance of polymer solar cell based on P3HT:$PC_{61}BM$ doped with Bis-AEP

D.C.	V_{OC} (V)	J_{SC} (mA/cm²)	FF	PCE (%)
0	0.61	10.35±0.09	0.58±0.00	3.67±0.04
0.5%	0.61	10.54±0.12	0.57±0.01	3.62±0.08
1%	0.60	10.37±0.14	0.55±0.01	3.46±0.08
3%	0.60	9.15±0.29	0.56±0.00	3.08±0.12
5%	0.60	9.05±0.20	0.57±0.00	3.09±0.08

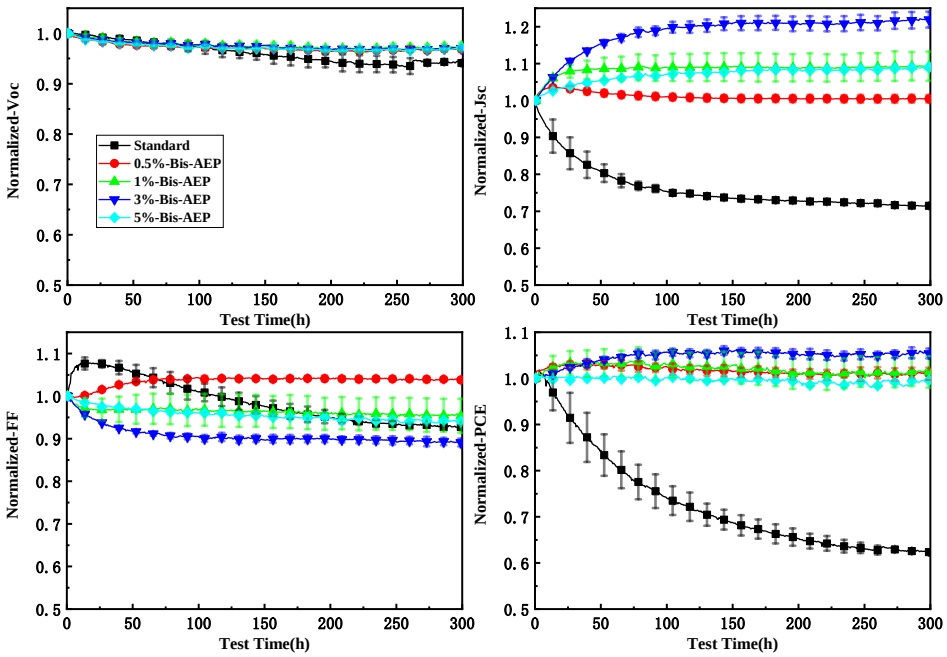


Figure S14. Degradation curves of polymer solar cell based on P3HT:$PC_{61}BM$ doped with Bis-AEP

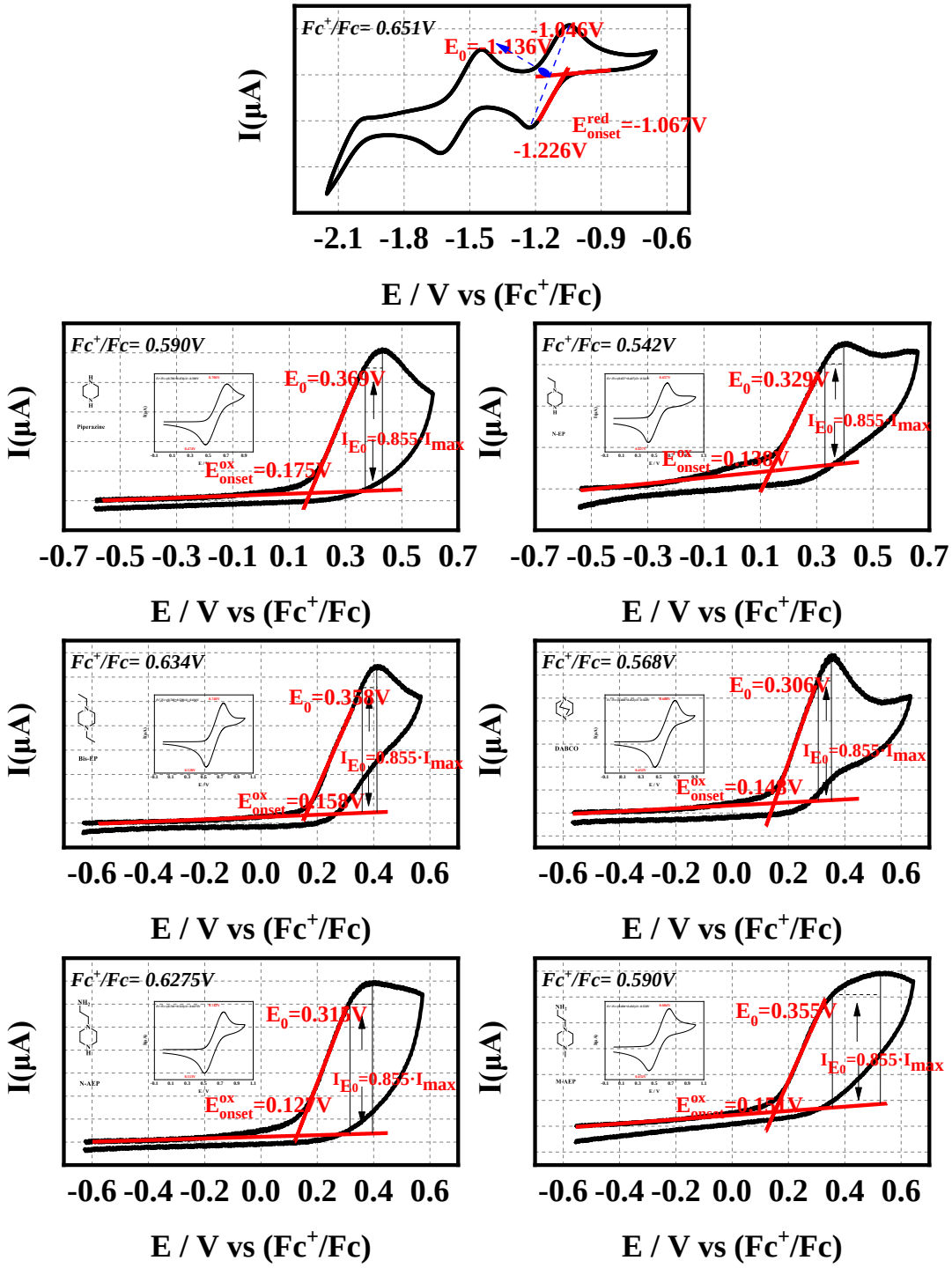


Figure S15. C-V curves of $PC_{61}BM$ and piperazine derivatives (without Bis-AEP because its poor solubility in DCM)

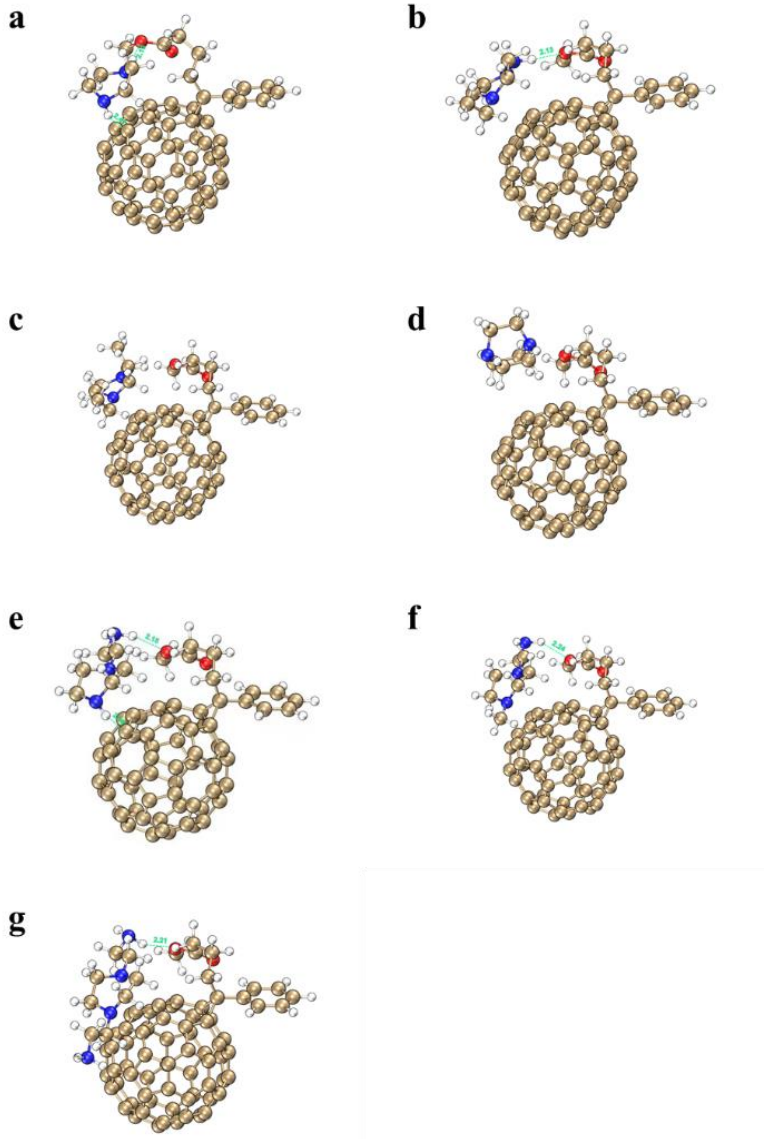


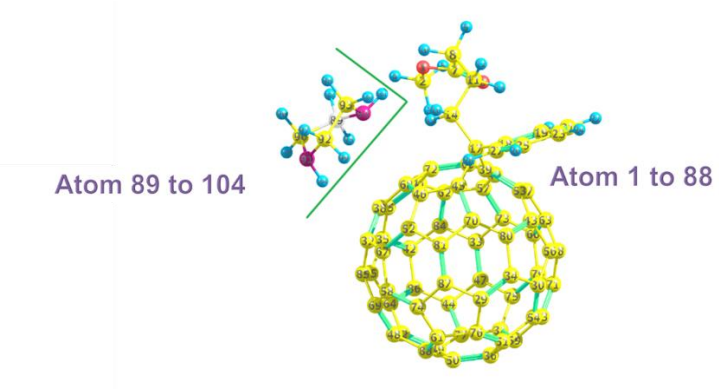
Figure S16. Optimal structure of $PC_{61}BM$-PZs compound: a) Piperazine; b) N-EP, c) Bis-EP, d) DABCO, e) N-AEP, f) M-AEP, g) Bis-AEP

Table S8. Calculated length of N-H···O-C bond between $PC_{61}BM$ and PZs

Sample	Piperazine	N-EP	Bis-EP	DABCO	N-AEP	M-AEP	Bis-AEP
d_1	2.10[a]	2.13[a]	2.50[b]	2.86[b]	2.15[a]	2.24[a]	2.21[a]
d_2	2.41[c]				2.30 [c]		

a: the length of N-H···O-C, in Å. b: the distance between O and the closest H-C of piperazine derivative; c: the length of N-H…π (except Bis-AEP because the result of N-H…π is too long, indicating such a bond is too weak)

Table S9. Mulliken charge on $PC_{61}BM$:piperazine adduct on the ground and excited states



Ground State					Excited State		
Atom	Element	Mulliken Charge			Atom	Element	Mulliken Charge
1	O	-0.3268	PCBM		1	O	-0.330067
2	C	0.182915			2	C	0.182054
3	H	0.048131			3	H	0.034272
4	H	0.033167			4	H	0.030354
5	H	0.035978			5	H	0.033876
6	O	-0.229392			6	O	-0.228589
7	C	0.152112			7	C	0.144834
8	C	0.060058			8	C	0.083945
9	H	0.034172			9	H	0.030068
10	H	0.008644			10	H	0.007094
11	C	0.021148			11	C	0.015846
12	H	0.007314			12	H	0.005065
13	H	0.023969			13	H	0.01507
14	C	0.174701			14	C	0.169235
15	H	0.007243			15	H	0.035091
16	H	-0.004651			16	H	-0.009411
17	C	-0.057186			17	C	-0.038548
18	C	0.016703			18	C	0.009696
19	C	0.005434			19	C	0.018947
20	H	0.000995			20	H	-0.014963
21	C	0.017103			21	C	0.017778
22	H	-0.015155			22	H	-0.015215
23	C	0.02806			23	C	0.02842
24	H	-0.013227			24	H	-0.01299
25	C	0.01897			25	C	0.019091
26	H	-0.015451			26	H	-0.015366
27	C	0.008727			27	C	0.011302
28	H	-0.020305			28	H	-0.020359
29	C	-0.011067			29	C	-0.006655

30	C	-0.008265			30	C	-0.010318
31	C	-0.002229			31	C	-0.001898
32	C	-0.044063			32	C	-0.038242
33	C	-0.004985			33	C	-0.004487
34	C	0.005952			34	C	0.00616
35	C	-0.013168			35	C	-0.007761
36	C	-0.002143			36	C	-0.000443
37	C	0.005985			37	C	-0.002572
38	C	0.109919			38	C	-0.019389
39	C	-0.141997			39	C	-0.170108
40	C	0.041463			40	C	0.001538
41	C	-0.01766			41	C	0.00239
42	C	-0.007619			42	C	-0.005292
43	C	0.010133			43	C	0.009624
44	C	-0.003948			44	C	0.004097
45	C	-0.150045			45	C	-0.157139
46	C	0.0346			46	C	0.057691
47	C	-0.00204			47	C	-0.010211
48	C	-0.004929			48	C	-0.011815
49	C	-0.004615			49	C	-0.007864
50	C	-0.00223			50	C	-0.002897
51	C	-0.004803			51	C	-0.013869
52	C	0.002857			52	C	-0.013423
53	C	0.023964			53	C	0.043158
54	C	-0.001023			54	C	0.007413
55	C	-0.031834			55	C	0.000469
56	C	0.004062			56	C	0.002952
57	C	-0.018997			57	C	-0.000735
58	C	-0.007004			58	C	-0.004617
59	C	-0.002681			59	C	-0.002152
60	C	0.059214			60	C	0.087333
61	C	-0.003329			61	C	0.000499
62	C	-0.027547			62	C	-0.02669
63	C	-0.015229			63	C	-0.01638
64	C	-0.007458			64	C	-0.004544
65	C	-0.004291			65	C	-0.00553
66	C	-0.003139			66	C	-0.004575
67	C	-0.0147			67	C	-0.02297
68	C	0.012542			68	C	0.034005
69	C	-0.001435			69	C	-0.009774
70	C	0.048581			70	C	0.056965
71	C	-0.004059			71	C	-0.010481
72	C	-0.012343			72	C	0.020641

73	C	-0.003749			73	C	-0.008202
74	C	-0.003444			74	C	-0.00775
75	C	-0.003168			75	C	-0.00097
76	C	-0.001938			76	C	-0.009865
77	C	-0.002182			77	C	-0.008257
78	C	-0.008243			78	C	-0.005211
79	C	-0.001191			79	C	-0.000127
80	C	0.001419			80	C	-0.000367
81	C	0.003796			81	C	-0.002584
82	C	-0.000331			82	C	0.004716
83	C	-0.003937			83	C	-0.012264
84	C	-0.000553			84	C	0.005467
85	C	-0.006345			85	C	0.007642
86	C	-0.001929			86	C	-0.004084
87	C	-0.012874			87	C	-0.01422
88	C	-0.001268			88	C	-0.000206
	Overall Charge on $PC_{61}BM$	-0.064163				Overall Charge on $PC_{61}BM$	-0.107648
89	C	0.14789	Piperazine		89	C	0.130901
90	C	0.090732			90	C	0.099814
91	N	-0.29022			91	N	-0.297588
92	C	0.181576			92	C	0.175791
93	C	0.071481			93	C	0.074563
94	N	-0.311956			94	N	-0.312942
95	H	0.003476			95	H	0.024636
96	H	-0.019777			96	H	-0.01331
97	H	-0.015093			97	H	-0.008048
98	H	-0.016999			98	H	-0.014907
99	H	-0.002606			99	H	-0.004358
100	H	0.000642			100	H	0.004552
101	H	0.130325			101	H	0.119774
102	H	0.106707			102	H	0.120939
103	H	0.004175			103	H	0.016
104	H	-0.016195			104	H	-0.00817
		0.064158					0.107647
	Mulliken Charge redistribution over excitation						-0.043485

Table S10. calculated stead state energy for $PC_{61}BM$ at different forms[a]

Photon induced electron transfer (PET)				Photon induced energy transfer (PEnT)			
E_{PCBM}	E_{PCBM^-}	$E_A^{w/o\ piperazine}$	ΔE_A	E_{PCBM}	E_{PCBM*}	$E_{Ex}^{w/o\ piperazine}$	ΔE_{Ex}
-2903.65758	-2903.74988	-0.09230[b]	-0.00554[d] (-3.47)[e]	-2903.65758	-2903.58906	0.06852[f]	-0.00055[h] (-0.34)[e]
$E_{PCBM-Pz}$	E_{PCBM^--Pz}	$\Delta E_A^{w\ piperazine}$		$E_{PCBM-Pz}$	$E_{PCBM*-Pz}$	$E_{Ex}^{w\ piperazine}$	
-3171.71683	-3171.81467	-0.09784[c]		-3171.71683	-3171.64886	0.06797[g]	

a: energy calculated by DFT method, in Hartree; b: electron affinity energy for $PC_{61}BM$ without piperazine; c: electron affinity energy for $PC_{61}BM$ with piperazine; d: electron affinity energy difference for $PC_{61}BM$ upon piperazine doping, ΔE_A ($PC_{61}BM$) = $E_A^{w\ piperazine}$ - $E_A^{w/o\ piperazine}$; e: energy in kcal/mol; f: excitation energy for $PC_{61}BM$ without piperazine; g: excitation energy for $PC_{61}BM$ with piperazine; h: excitation energy difference for $PC_{61}BM$ upon piperazine doping, ΔE_{Ex} ($PC_{61}BM$) = $E_{Ex}^{w\ piperazine} - E_{Ex}^{w/o\ piperazine}$