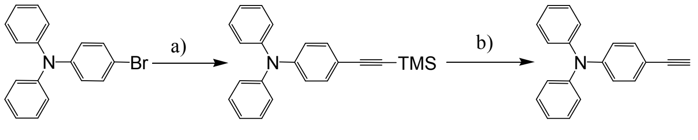
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for

Co-sensitization of N719 with polyphenylene from Bergman cyclization of maleimide-based enediyne for dye-sensitized solar cells

Luhua Dong[a], Zhiwei Zheng[b], Youfu Wang[a], Xing Li[b], Jianli Hua*[b], Aiguo Hu*[a]

Synthesis



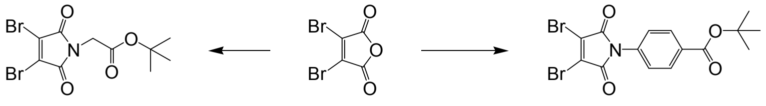
1 **2**

Compound 1. Compound **1** was synthesized according to the methods from literature[1]. 4-Bromotriphenylamine (8.1050 g, 25 mmol), CuI (0.5714 g, 3 mmol), and $Pd(PPh_3)_2Cl_2$ (0.5264 g, 0.75 mmol), PPh_3 (0.3935 g, 1.5 mmol) were mixed in a 350 mL Schlenk flask. Then degassed toluene (150 ml), piperidine (20 mL, 20 mmol) and trimethylsilylacetylene (TMSA) (17.8 mL, 125 mmol) were added successively under a nitrogen atmosphere. The reaction mixture was stirred at 90 ºC overnight. The dark brown resulting solution was concentrated and partitioned with saturated aqueous NaCl and dichloromethane (DCM), and the organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under vacuum, the crude product was purified through column chromatography (200~300 mesh silica, PE : DCM = 7 : 1) to yield a yellow oil (7.34 g, 86%). ^1H NMR (DMSO-d^6, 400 MHz, ppm): 7.33 (dd, J = 7.3 Hz, 7.2 Hz, 4H); 7.29 (d, J = 8.6 Hz, 2H); 7.10 (t, J = 7.3 Hz, 2H); 7.05 (d, J = 7.2 Hz, 4H); 6.82 (d, J = 8.6 Hz, 2H); 0.20 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d^6): 147.7; 146.3; 132.7; 129.6; 125.0; 124.0; 120.8; 114.5; 105.5; 92.7; 0.1. HR-MS (ESI): m/z calcd. for $C_{26}H_{29}NSi$ $(M)^+$: 341.1600; found: 341.1669.

Synthesis of compound 2. To a stirred solution of the trimethylsilyl-protected acetylene derivatives **1** (6.82 g, 20 mmol) and p-toluenesulfonic acid (PTSA, 3.80 g, 20 mmol) in THF (50 mL) was added the solution of tetrabutylammonium fluoride

(TBAF, 12.6204 g, 40 mmol) in THF (50 mL). The mixture was stirred for 30 min with ice-water bath and then concentrated. The viscous liquid was diluted with DCM and washed with water for several times. The organic layer was dried over anhydrous $MgSO_4$, and then filtered and concentrated under vacuum. The crude compound was purified through column chromatography (200~300 mesh silica, PE : DCM=10 : 1) to yield a white solid (4.84 g, 90%). ^{1}H-NMR (DMSO-d_6, 400 Hz, ppm): 7.33 (m, 6H), 7.10 (t, J = 7.2 Hz, 2H), 7.05 (d, J = 7.2 Hz, 4H), 6.86 (d, J = 8.5 Hz, 2H), 4.05 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): 148.3; 146.9; 133.3; 130.2; 125.4; 124.5; 121.7; 114.7; 84.1; 80.1. HR-MS (ESI): m/z calcd. for $C_{20}H_{15}N$ $(M)^+$: 269.1204, found, 269.1205.

Synthesis of compound 3[2]. Maleic anhydride (9.00 g, 91.8 mmol) and $AlCl_3$ (0.1880 g, 1.41 mmol) were added in a 100 mL sealed tube. Then liquid bromine (9 mL) was added under a nitrogen atmosphere. The reaction mixture was stirred at 120 ºC for 16 h. The product was dissolved in ethyl acetate and filtered. The residue was washed with ethyl acetate and the solvent of the filtrate was removed under vacuum to give the product as a white solid (21.71 g, 93%).



4 **5**

Synthesis of compound 4. tert-Butyl glycinate (2.73 mL, 20 mmol) was dissolved in acetic acid (30 mL) in a 200 mL flask, then 30 mL acetic acid solution of compound 3 (5.12 g, 20.2 mmol) was added. The mixture was stirred at room temperature for 24 h and then concentrated. The light yellow oily liquid was partitioned with saturated aqueous $NaHCO_3$ and ethyl acetate (EtOAc), and the organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under vacuum, the crude product was purified through column chromatography (200~300 mesh silica, PE : EtOAc = 10 : 1) to yield a white solid (5.22 g, 71%). ^{1}H-NMR ($CDCl_3$, 400 Hz, ppm): 4.25 (s, 2H), 1.46 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 164.5; 162.4; 128.8; 82.5; 39.9; 27.0. HR-MS (ESI): m/z calcd. for $C_{10}H_{15}Br_2N_2O_4$ $(M + NH_4)^+$: 384.9399, found, 384.9404.

Synthesis of compound 5. tert-Butyl 4-aminobenzoate (1.93 g, 10 mmol) was dissolved in acetic acid (20 mL) in a 100 mL flask, then 20 mL acetic acid solution of compound 3 (2.56 g, 10.1 mmol) was added. The mixture was stirred at room temperature for 24 h and then concentrated. The light yellow oily liquid was partitioned with saturated aqueous $NaHCO_3$ and EtOAc, and the organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under vacuum, the crude product was purified through column chromatography (200~300 mesh silica, PE : EtOAc = 10 : 1) to yield a white solid (3.41 g, 79%). ^{1}H-NMR ($CDCl_3$, 400 Hz, ppm): 8.09 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 1.60 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 164.6; 162.4; 134.3; 131.7; 130.4; 130.0; 125.1; 81.6; 28.1. HR-MS (ESI): m/z calcd. for $C_{15}H_{13}Br_2NO_4$ $(M)^+$: 430.9191, found, 430.9283.

Synthesis of compound 8. Compound 7 (0.20 g, 0.25 mmol) in a 50 mL flask reacted with trifluoroacetic acid (10 mL) under 0 ºC. After removal of the solvent under vacuum, the product compound 8 (0.185 g, yield 99%) was got without further purification. HR-MS(ESI): m/z calcd. for $C_{51}H_{33}N_3O_4$ $(M)^+$: 751.2471, found: 751.2470

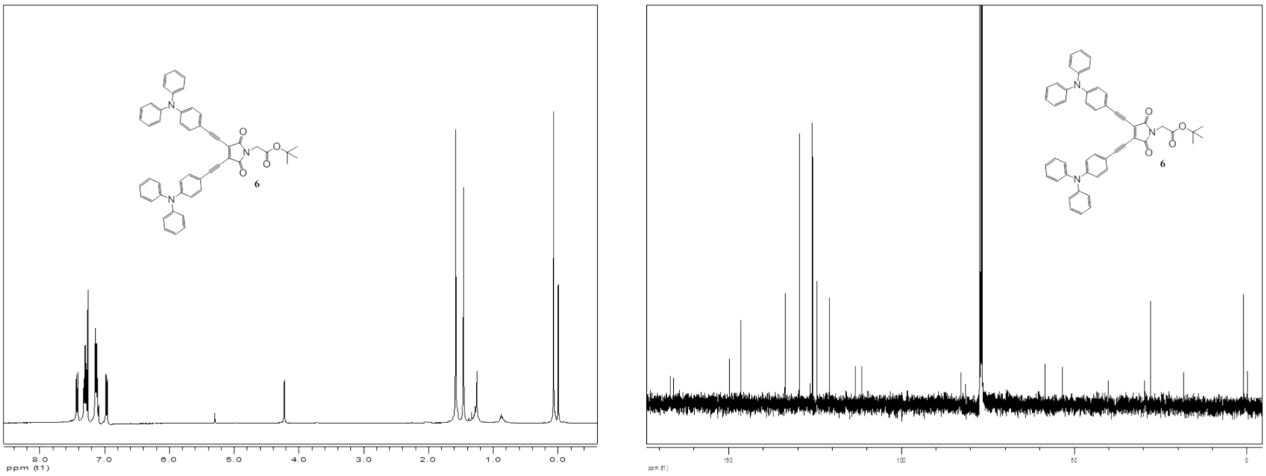


Fig.S1 ^{1}H-NMR and ^{13}C NMR spectra of compound **6**.

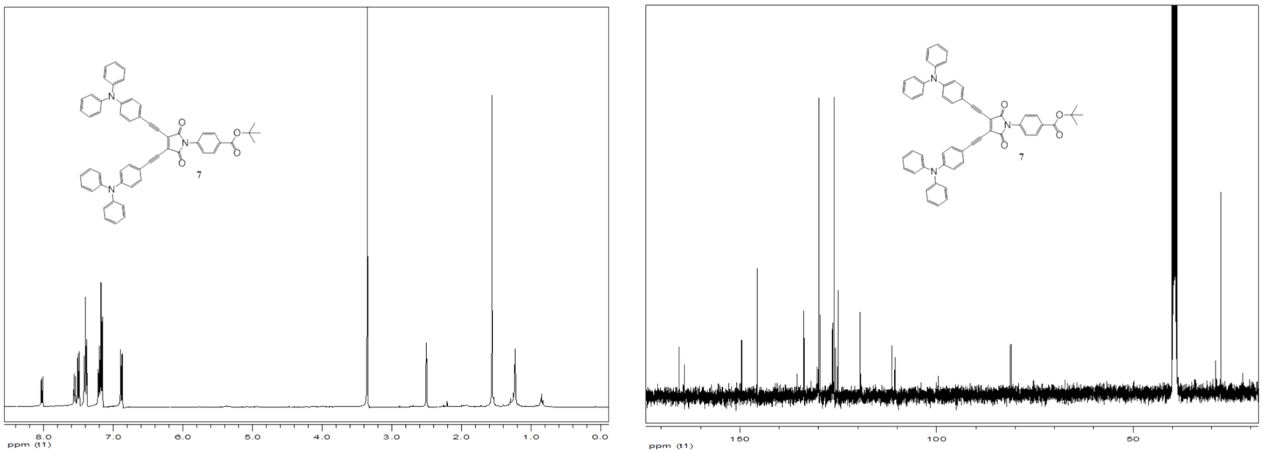


Fig.S2 ^{1}H-NMR and ^{13}C NMR spectra of compound **7**.

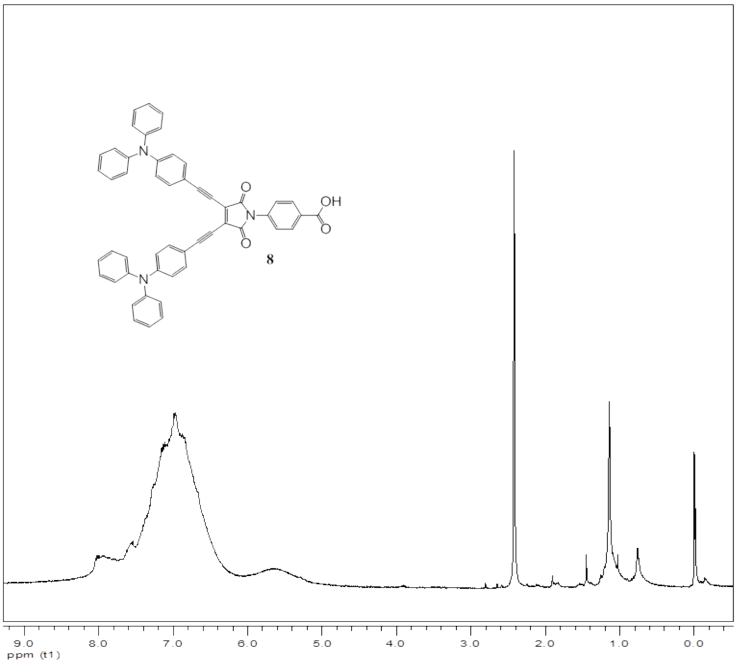


Fig. S3. ^{1}H-NMR spectrum of compound **8**.

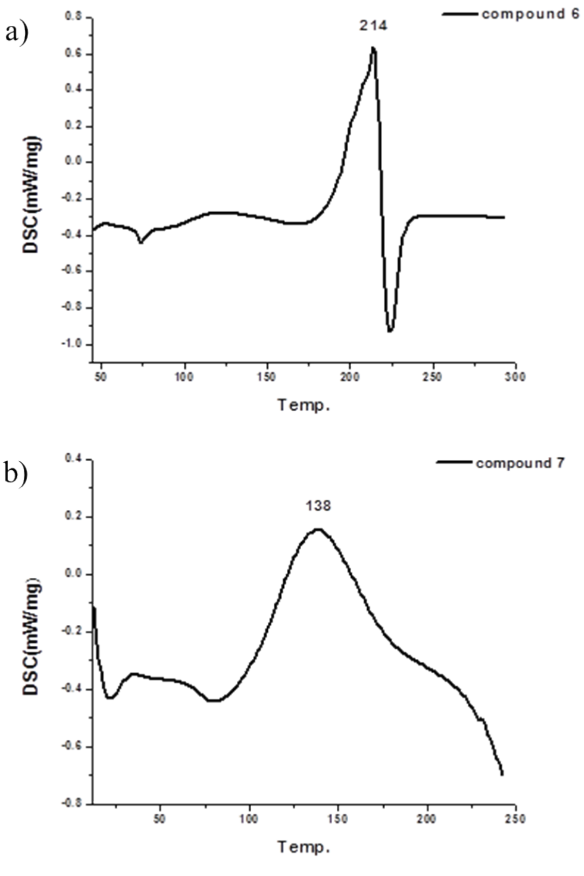


Fig. S4. DSC curves of enediyne compounds **6** (a) and **7** (b).

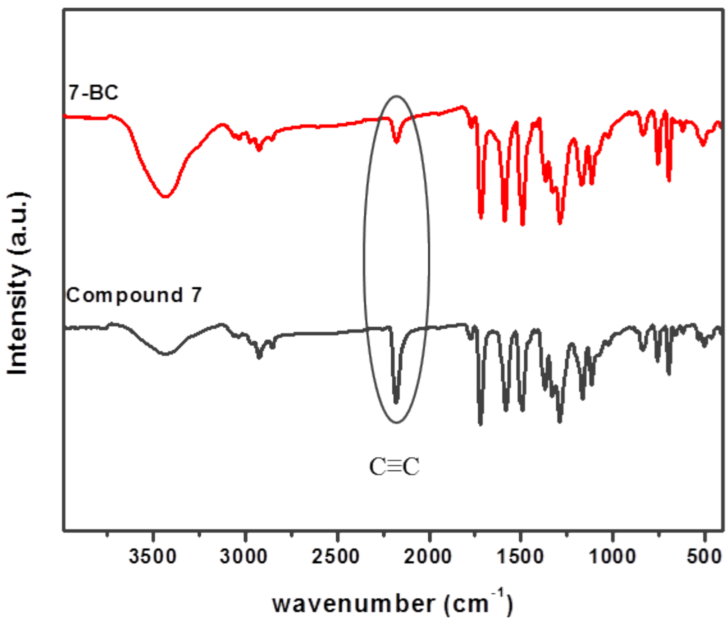


Fig.S5 FT-IR spectra of compound **7** and **7-BC**.

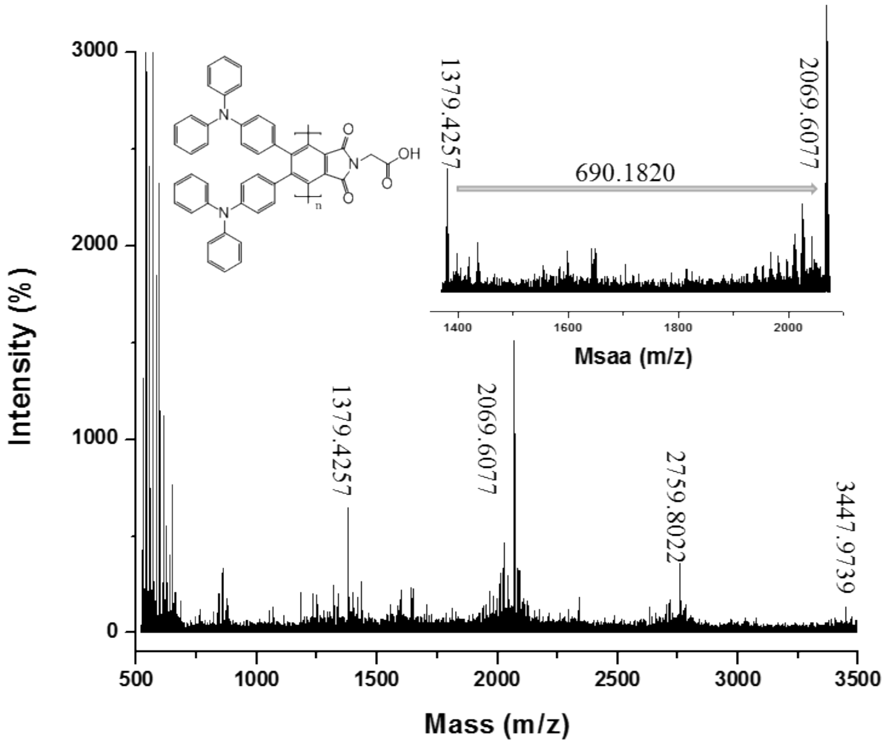


Fig.S6 MALDI-TOF mass spectrum of the oligomer part of **6-BC**.

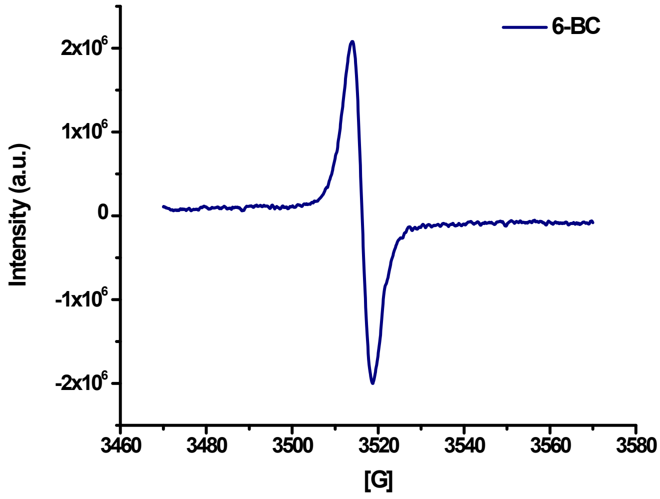


Fig. S7. EPR spectrum of **6-BC** in $CHCl_3$.

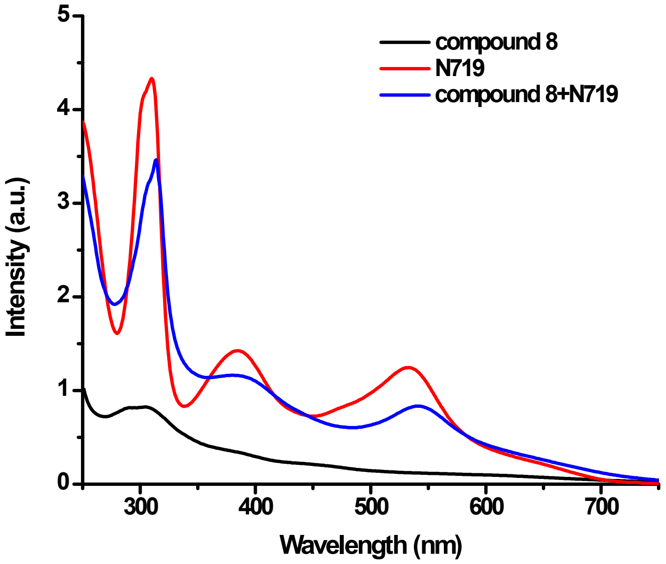


Fig. S8. UV-Vis absorption spectra of compound **8** in $CHCl_3$, **N719** and compound **8+N719** in mix solution of acetonitrile and n-butyl alcohol (v/v=1:1).

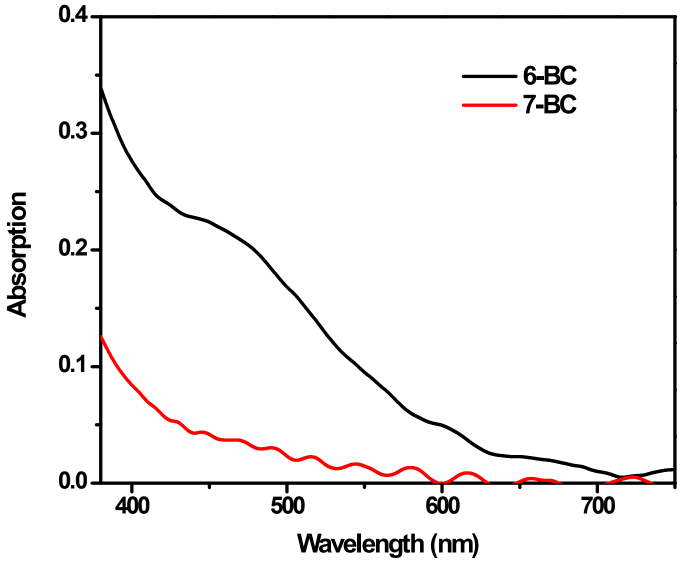


Fig.S9 UV-Vis absorption spectra of **6-BC** and **7-BC** on thin TiO_2 film (4 μm).

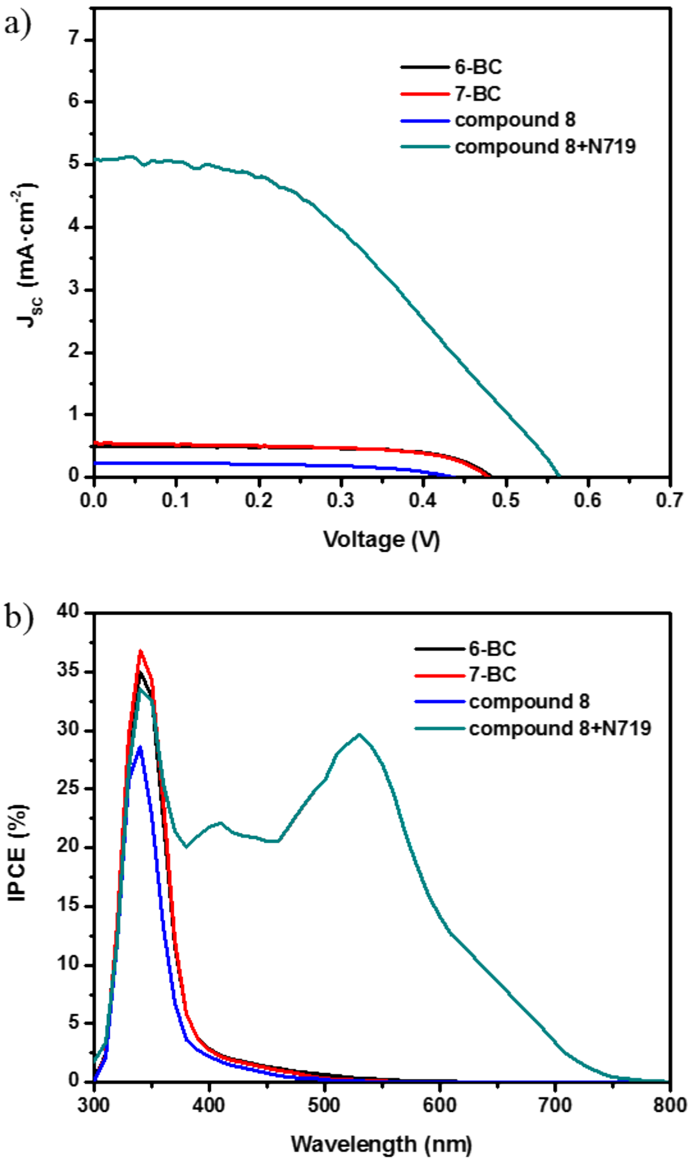


Fig.S10 a) J-V curves and b) IPCE spectra of DSSCs sensitized with **6-BC**, **7-BC**, compound **8** and compound **8**+**N719**.

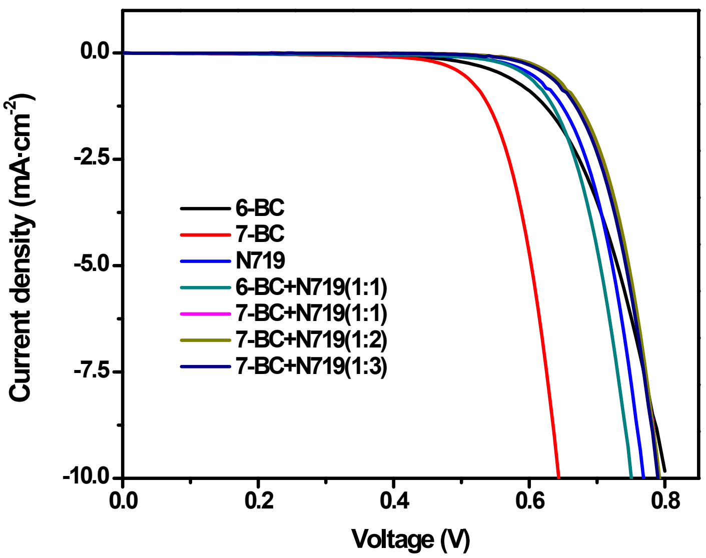


Fig.S11 Dark current- voltage curves of DSSCs devices based on **6-BC**, **7-BC**, **N719**, **6-BC+N719**(1:1), **7-BC+N719**(1:1, 1:2, 1:3)

References:

1. M. Planells, A. Abate, D. J. Hollman, S. D. Stranks, V. Bharti, J. Gaur, D. Mohanty, S. Chand, H. J. Snaith and N. Robertson, *J. Mater. Chem. A*, 2013, **1**, 6949-6960.
2. M. Dubernet, V. Caubert, J. Guillard and M.-C. Viaud-Massuard, *Tetrahedron*, 2005, **61**, 4585-4593.