Electronic Supplementary Information (ESI)

Cu(II)-Porphyrin based Near-infrared Molecules: Synthesis, Characterization and Photovoltaic Application

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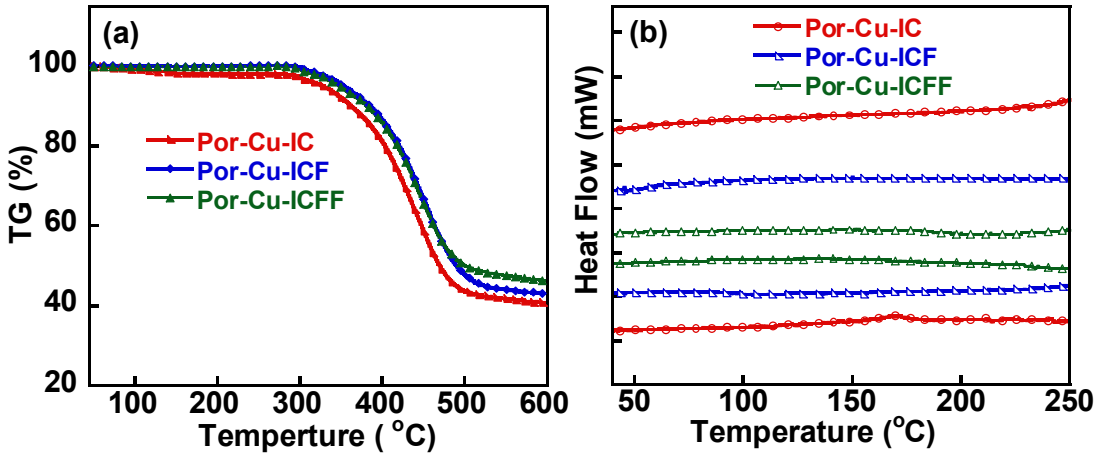

Fig. S1. The TG and DSC curves of the three porphyrin-based acceptors.

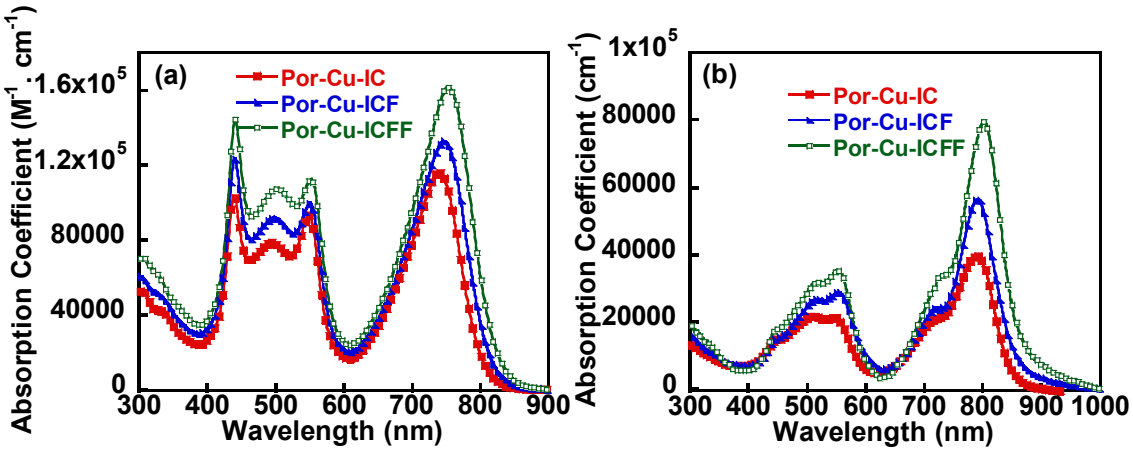

Fig. S2. UV-vis absorption coefficient spectra of the two acceptors in chloroform solution (a) and in the film state (b).

Table S1. Optical properties of the three porphyrin-based acceptors.

Acceptors	UV-vis in solution			UV-vis as thin films			
	λ_{max}/nm	λ_{onset}/nm	ε (10^5 M^{-1} cm^{-1})	λ_{max}/nm	λ_{onset}/nm	E_g^{opt}/eV	ε (10^5 cm^{-1})
Por-Cu-IC	737	820	1.16	788	864	1.44	0.39
Por-Cu-ICF	746	828	1.33	790	880	1.41	0.56
Por-Cu-ICFF	754	838	1.61	804	898	1.38	0.79

Table S2. Photovoltaic properties of the OSCs based on PBDB-T as donor and Por-Cu-IC or Por-Cu-ICF or Por-Cu-ICFF as the acceptor under AM 1.5 G at 100 mW cm^{-2}.

Acceptor	D:A (w/w)	Py additive	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	*PCE* (%)
Por-Cu-ICFF	1.5:1	w/o	0.76	6.09	36.37	1.69
Por-Cu-ICFF	1:1	w/o	0.76	5.97	39.27	1.79
Por-Cu-ICFF	1:1.5	w/o	0.76	5.79	38.98	1.71
Por-Cu-ICFF	1:1	0.5 %	0.79	7.30	42.37	2.44
Por-Cu-ICFF	1:1	1 %	0.79	5.89	43.36	2.01
Por-Cu-ICF	1:1	0.5 %	0.81	5.03	45.66	1.85
Por-Cu-IC	1:1	0.5 %	0.82	1.58	39.81	0.52
Por-Cu-ICFF ： ITIC (1:1)	1:1	0.5%	0.82	7.82	46.71	3.13

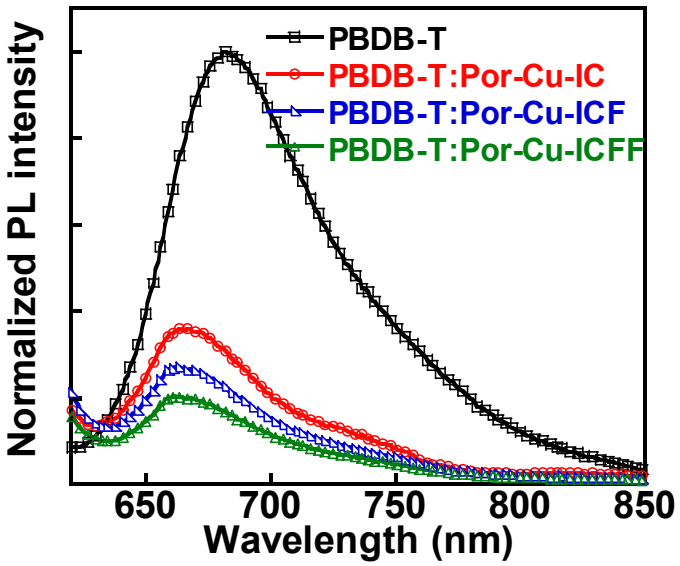

Fig. S3. PL spectra of thin films: PBDB-T, PBDB-T: Por-Cu-IC, PBDB-T: Por-Cu-ICF and PBDB-T: Por-Cu-ICFF, (1:1, with 0.5% pyridine)

Table S3. Electron/hole mobility for PBDB-T: acceptor blend films.

Film	μ_e (cm^2 V^{-1} s^{-1})	μ_h (cm^2 V^{-1} s^{-1})	μ_h/ μ_e
PBDB-T: Por-Cu-IC	6.19×10^{-6}	3.76×10^{-4}	60.7
PBDB-T: Por-Cu-ICF	8.34×10^{-6}	3.29×10^{-4}	39.4
PBDB-T: Por-Cu-ICFF	1.32×10^{-5}	2.85×10^{-4}	21.6

Table S4. Stability tests under continuous 1 sun illumination in ambient environment for the PBDB-T:Por-Cu-ICFF blend devices.

Time (h)	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	*PCE* (%)
0	0.80	7.52	43.70	2.64
1	0.80	7.23	43.51	2.51
2	0.80	7.26	43.22	2.52
5	0.80	7.34	43.30	2.54
12	0.80	7.33	41.71	2.45
24	0.80	7.11	42.38	2.39
48	0.80	7.15	41.17	2.35
72	0.80	7.06	39.94	2.26

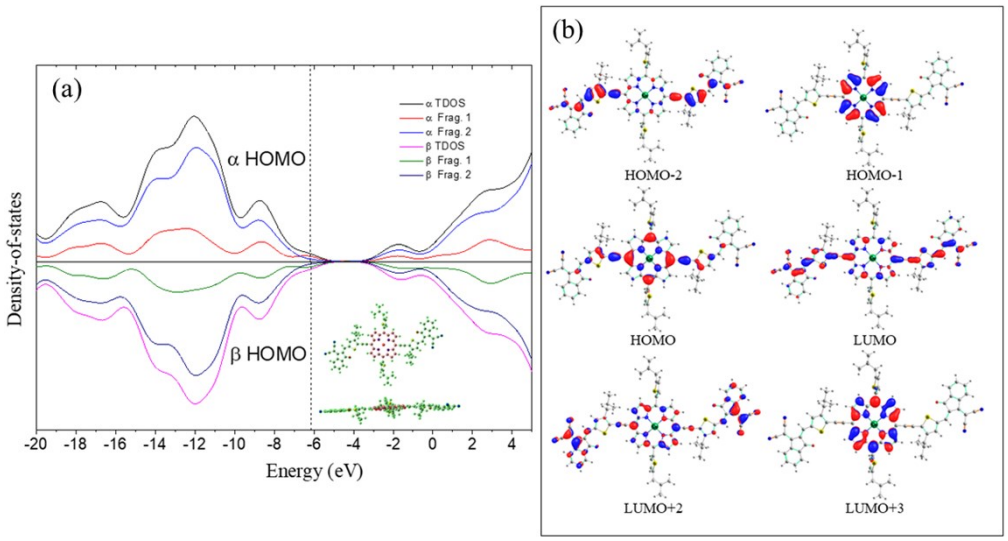

Fig. S4 (a) The total density of states (TDOS) of alpha and beta spin of Por-Cu-IC, along with the partial DOSs (PDOS) of two fragments in Por-Cu-IC. The definition of the two fragments were shown as different colors (red for Frag. 1 and green for Frag. 2) in the lower right corner. The optimized molecular geometry of Por-Cu-IC was shown in the lower right corner. (b) The distributions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), along with those of HOMO-2, HOMO-1, LUMO+2, and LUMO+3.

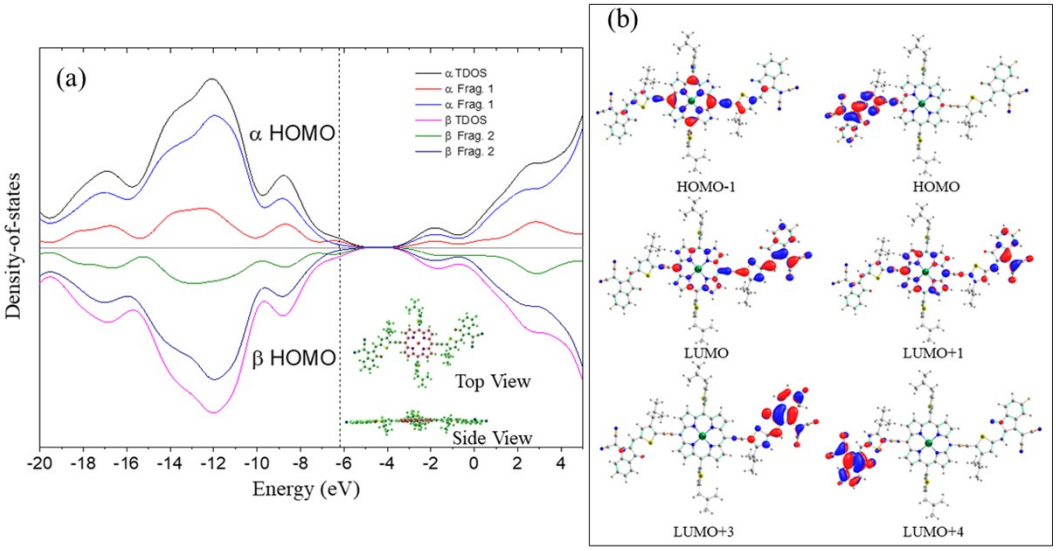

Fig. S5 (a) The total density of states (TDOS) of alpha and beta spin of Por-Cu-ICF, along with the partial DOSs (PDOS) of two fragments in Por-Cu-ICF. The definition of the two fragments were shown as different colors (red for Frag. 1 and green for Frag. 2) in the lower right corner. The optimized molecular geometry of Por-Cu-ICF was shown in the lower right corner. (b) The distributions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), along with those of HOMO-1, LUMO, LUMO+3, and LUMO+4.

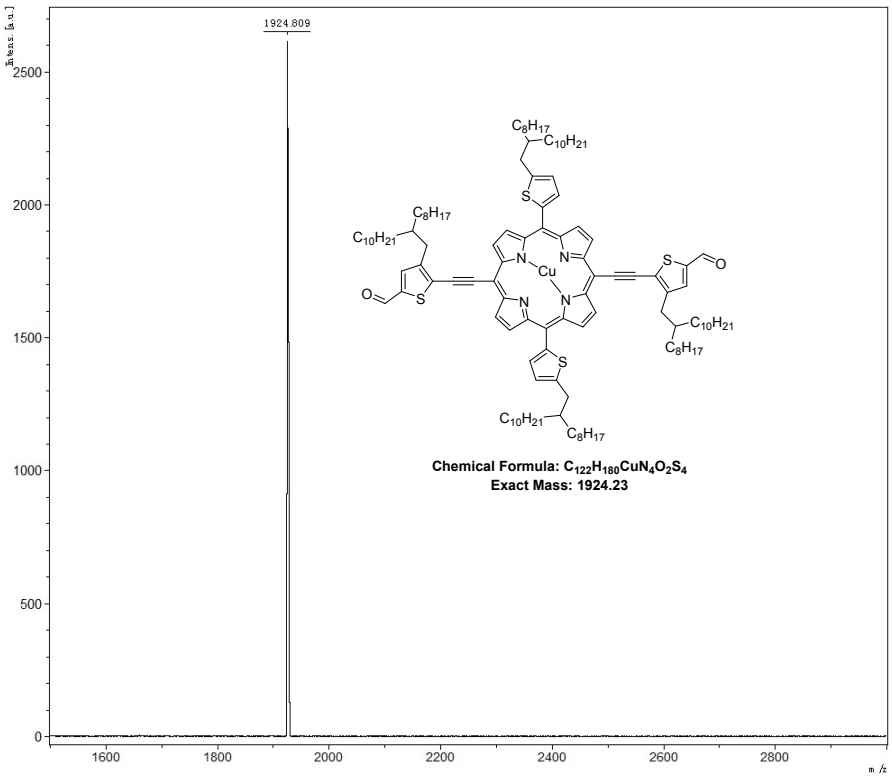

Fig. S6. Mass (MALDI-TOF) spectrum of **Por-Cu-CHO**.

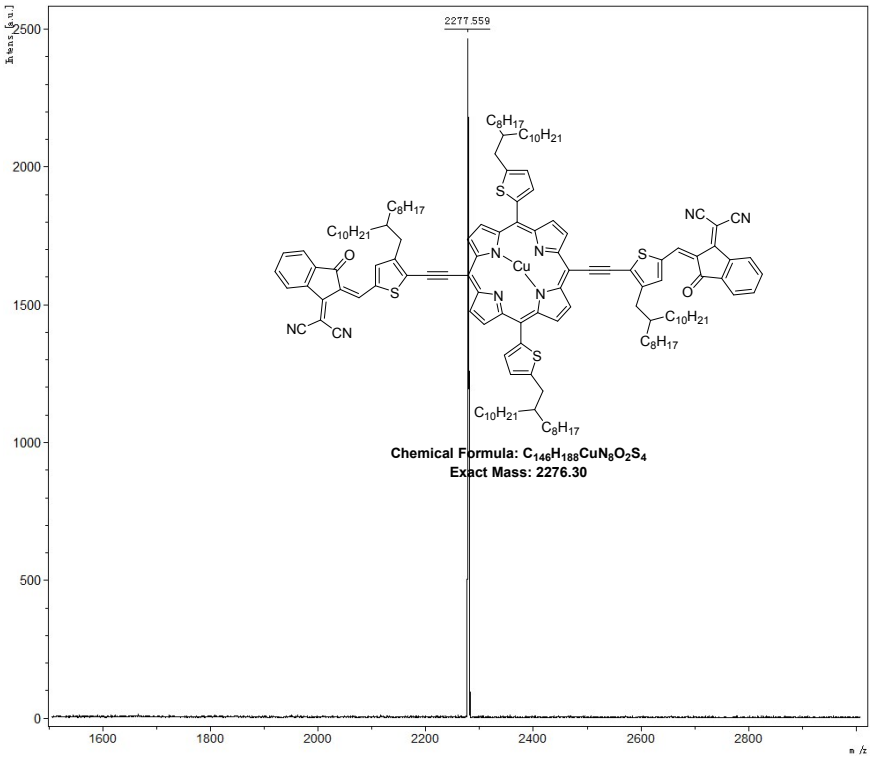

Fig. S7. Mass (MALDI-TOF) spectrum of **Por-Cu-IC**.

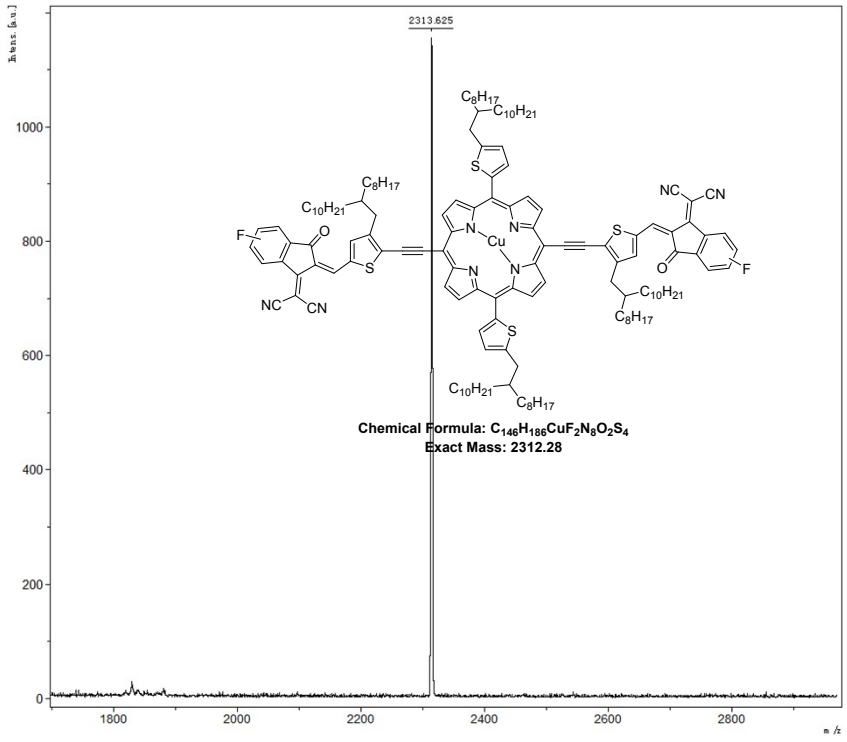

Fig. S8. Mass (MALDI-TOF) spectrum of **Por-Cu-ICF**.

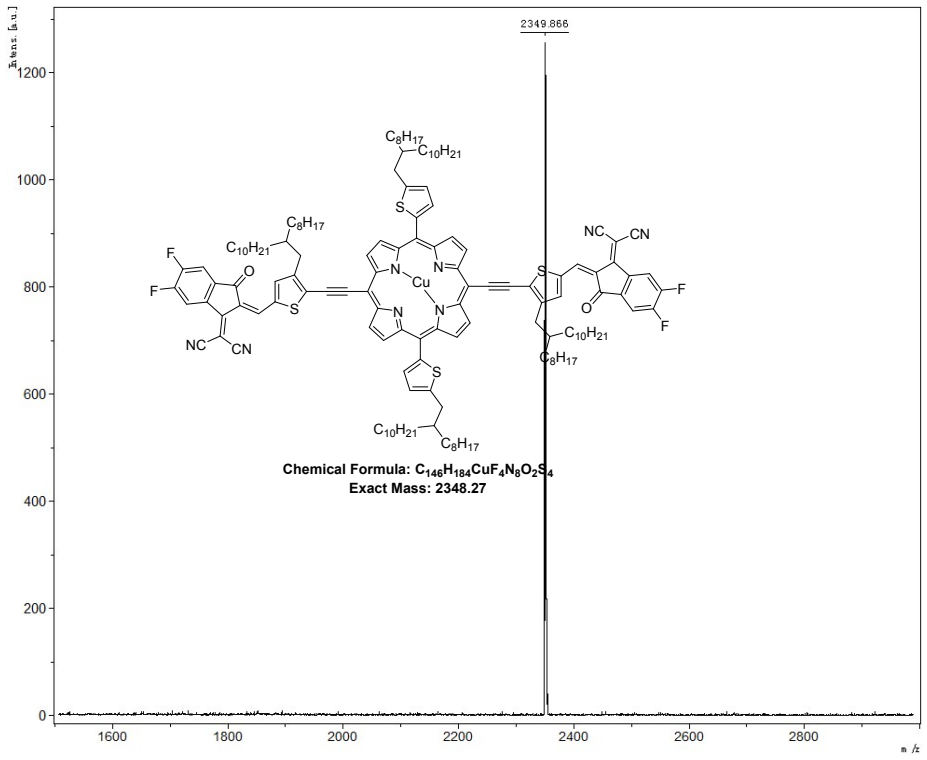

Fig. S9. Mass (MALDI-TOF) spectrum of **Por-Cu-ICFF**.