

Supporting Information

Carbazol-Phenyl-Phenothiazin-Based Sensitizers for Dye-Sensitized Solar Cells

Yunfei Jiao ^{a, b}, Shuaishuai Liu ^a, Zhongjin Shen ^{b, *}, Le Mao ^a, Yongjie Ding ^a, Dan Ren ^b, Felix Thomas Eickemeyer ^b, Lukas Pfeifer ^b, Dapeng Cao ^a, Wenjuan Xu ^a, Juan Song ^a, Baoxiu Mi ^{a, **}, Zhiqiang Gao ^a, Shaik M. Zakeeruddin ^b, Wei Huang ^{a, c, ***}, Michael Grätzel ^{b, ****}

^a State Key Laboratory of Organic Electronics and Information Displays (SKLOEID), Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications (NJUPT), 9 Wenyuan Road, Nanjing 210023, China

^b Laboratory of Photonics and Interfaces (LPI), Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne 1015, Switzerland

^c Frontiers Science Center for Flexible Electronics (FSCFE), MIIT Key Laboratory of Flexible Electronics (KLoFE), Northwestern Polytechnical University (NPU), 127 West Youyi Road, Xi'an 710072, China

* E-mail: zhongjin.shen@epfl.ch

** E-mail: iambxmi@njupt.edu.cn

*** E-mail: wei-huang@njtech.edu.cn

**** E-mail: michael.gratzel@epfl.ch

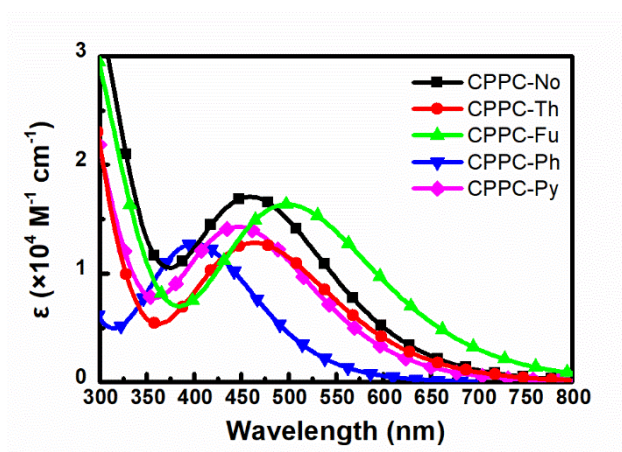


Fig. S1. Calculated absorption spectra of **CPPC** dyes.

Table S1 Dipole moments of **CPPC** dyes.

Dye	μ_{Tot}	μ_x	μ_y	μ_z
CPPC-No	8.8147	2.7759	8.3646	-0.1631
CPPC-Th	9.1231	-6.6880	6.1779	-0.5764
CPPC-Fu	15.3569	-3.4627	14.9611	0.0362
CPPC-Ph	9.1135	4.9464	7.6399	0.4649
CPPC-Py	9.8406	-3.9134	9.0271	-0.1778

Table S2 Photovoltaic parameters of the devices based on **CPPC-Fu** dyes with different concentrations of LiI.

Batch	LiI (M)	P_{in} (mW cm ⁻²)	J_{SC} (mA cm ⁻²)	V_{OC} (mV)	FF	PCE (%)	Normalization
1	0	99.9	10.11	783.2	0.803	6.34	0.92
		99.8	9.88	788.3	0.810	6.31	0.92
	0.05	100.1	10.10	777.4	0.811	6.36	0.93
		99.9	10.97	773.9	0.776	6.59	0.96
	0.1	99.9	11.04	763.4	0.773	6.52	0.95
		99.9	10.85	762.3	0.785	6.5	0.95
	0.15	99.8	11.40	735.7	0.777	6.53	0.95
		99.8	10.86	738.4	0.802	6.45	0.94
	0.2	99.8	11.44	750.8	0.79	6.8	0.99
		99.7	11.73	752.3	0.775	6.86	1.00
2	0.2	98.8	12.36	736.7	0.646	5.96	0.98
		98.8	12.50	733.1	0.650	6.07	1.00
	0.4	98.8	13.38	708.4	0.628	6.02	0.99
		98.7	13.15	715.3	0.625	5.96	0.98
	0.6	98.8	12.90	697.6	0.617	5.61	0.92
		98.7	13.70	690.6	0.572	5.48	0.90

0.8	98.7	13.63	687.6	0.557	5.29	0.87
	98.8	13.58	690.3	0.627	5.95	0.98
1.0	98.7	14.17	667.2	0.586	5.61	0.92
	98.6	14.23	671.0	0.527	5.10	0.84

Z960 (1 M DMII, 0.05 M LiI, 0.03 M I₂, 0.5 M tBP and 0.1 M GNCS in ACN) was used as reference electrolyte during device optimization. The concentrations of the components in Z960 with the exception of LiI were proven to be the optimal in this work. Two batches of devices with different concentrations of LiI were made independently. 0.2 M LiI was selected based on the normalized *PCE*, four times as much as in Z960 (0.05 M LiI). Compared with the devices using Z960, the *V*_{OC} and *FF* were decreased a little bit, on the contrary, for *J*_{SC} a big increase was observed.

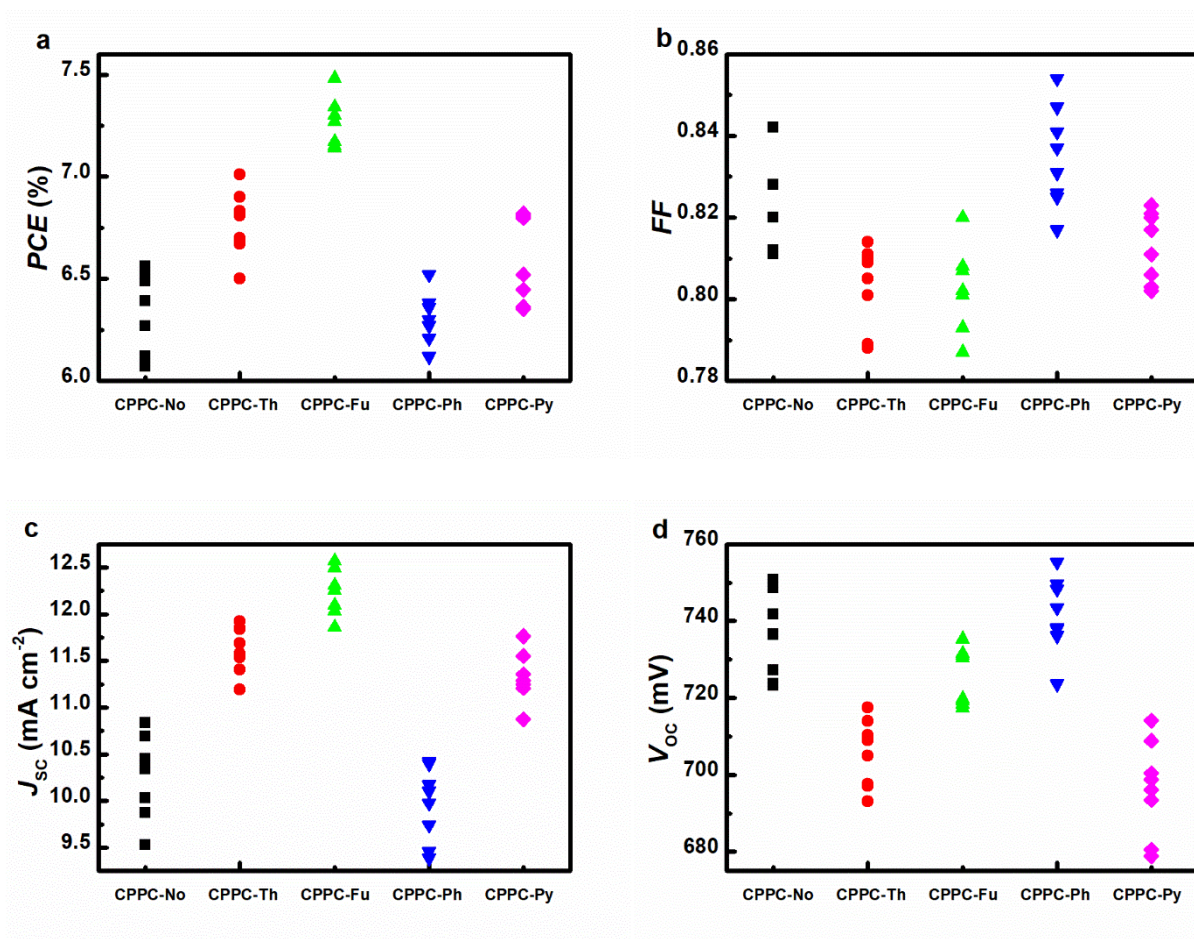
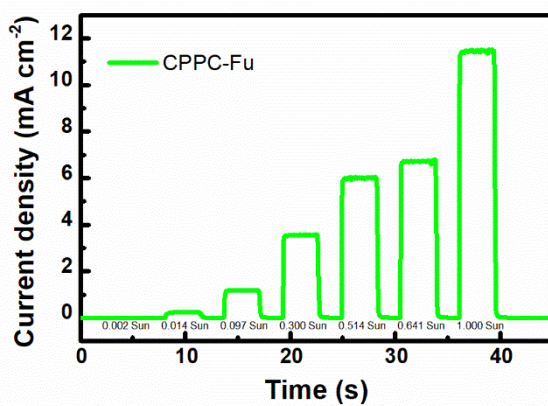
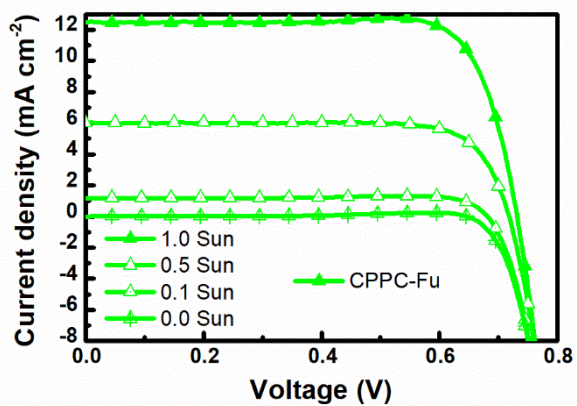
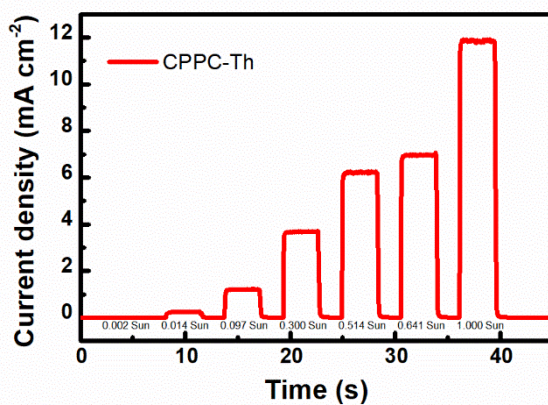
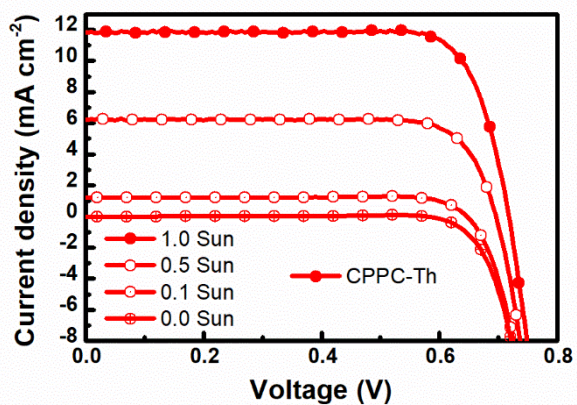
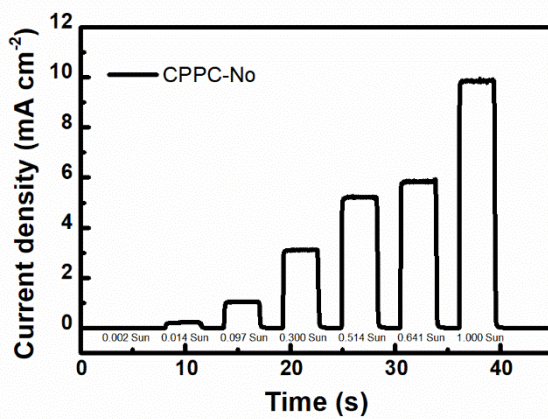
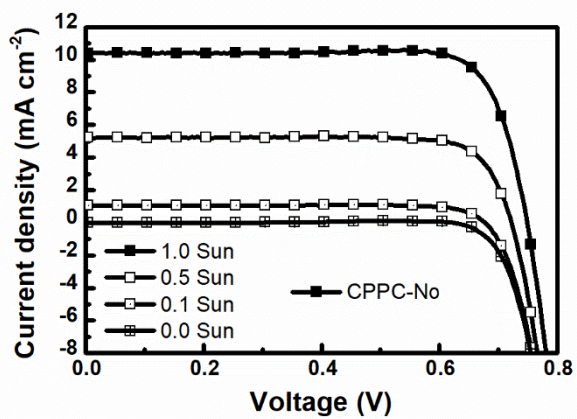


Fig. S2. Statistical data (a) *PCE*, (b) *FF*, (c) *J*_{SC} and (d) *V*_{OC} based on 8 cells for each dye.



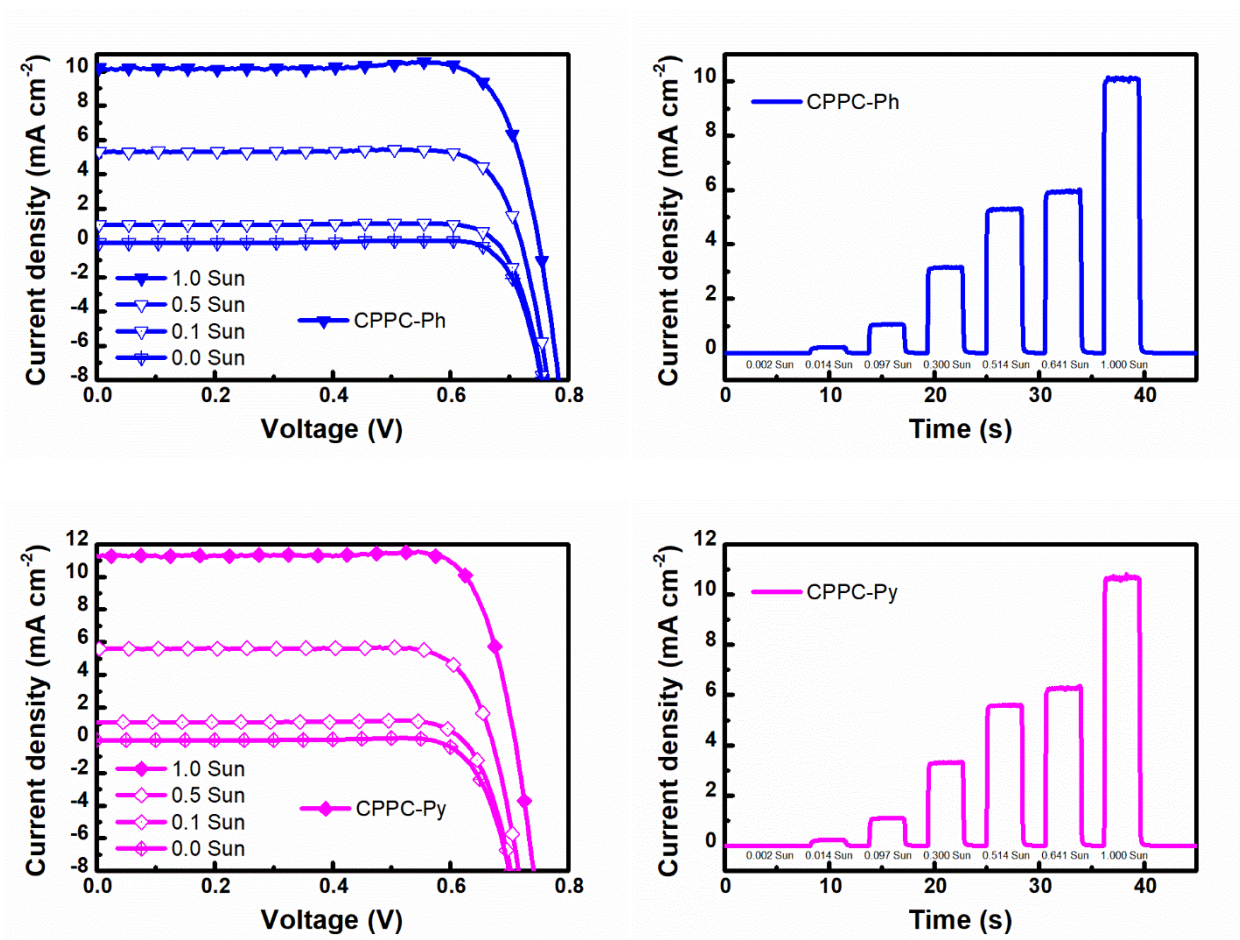


Fig. S3. (left) I-V curves measured under different light intensities and (right) current dynamic plots of the DSSCs based on CPPC dyes.

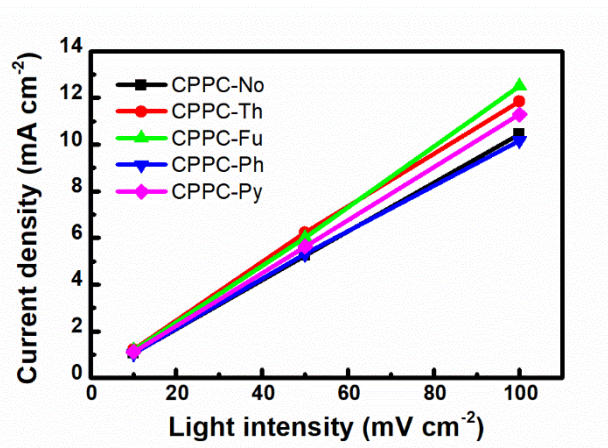


Fig. S4. Light intensity - current density dependence plots of the devices based on CPPC dyes.

Table S3 Photovoltaic parameters of the devices based on CPPC dyes under different light intensities.

Dye	P_{in} (mW cm ⁻²)	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	PCE (%)
CPPC-No	100	10.45	748.63	0.81	6.56

	50	5.25	721.83	0.80	5.97
	10	1.06	677.07	0.82	5.90
	100	11.84	717.49	0.80	7.01
CPPC-Th	50	6.23	695.53	0.80	6.80
	10	1.22	646.74	0.82	6.47
	100	12.50	731.54	0.80	7.48
CPPC-Fu	50	6.00	717.52	0.78	6.65
	10	1.19	680.86	0.80	6.48
	100	10.17	749.61	0.83	6.52
CPPC-Ph	50	5.31	719.60	0.83	6.24
	10	1.05	678.36	0.82	5.84
	100	11.29	708.86	0.82	6.82
CPPC-Py	50	5.63	669.95	0.81	6.02
	10	1.11	621.11	0.82	5.65

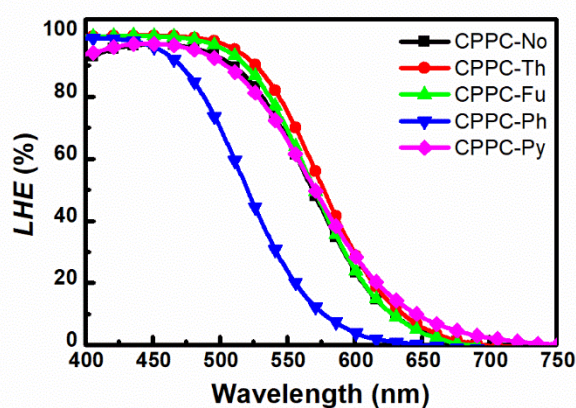


Fig. S5. *LHE* spectra of the dye-grafted TiO₂ films of CPPC dyes.

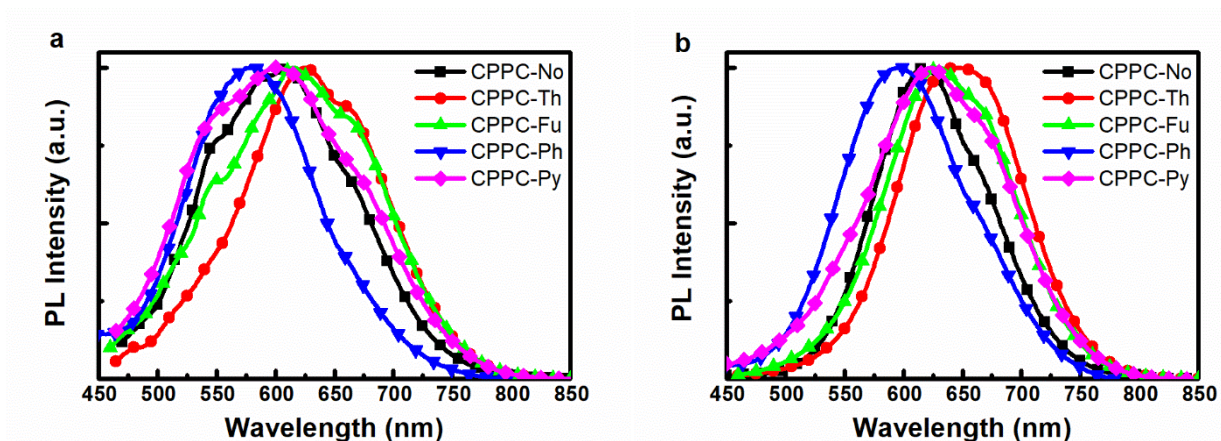


Fig. S6. Steady-state photoluminescence spectra of CPPC dyes (a) on TiO₂ and (b) Al₂O₃ films.

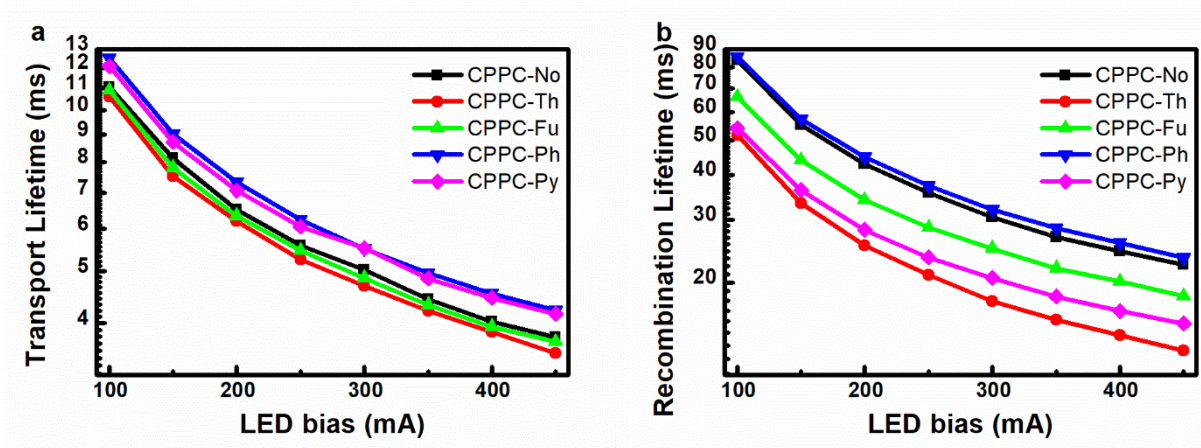
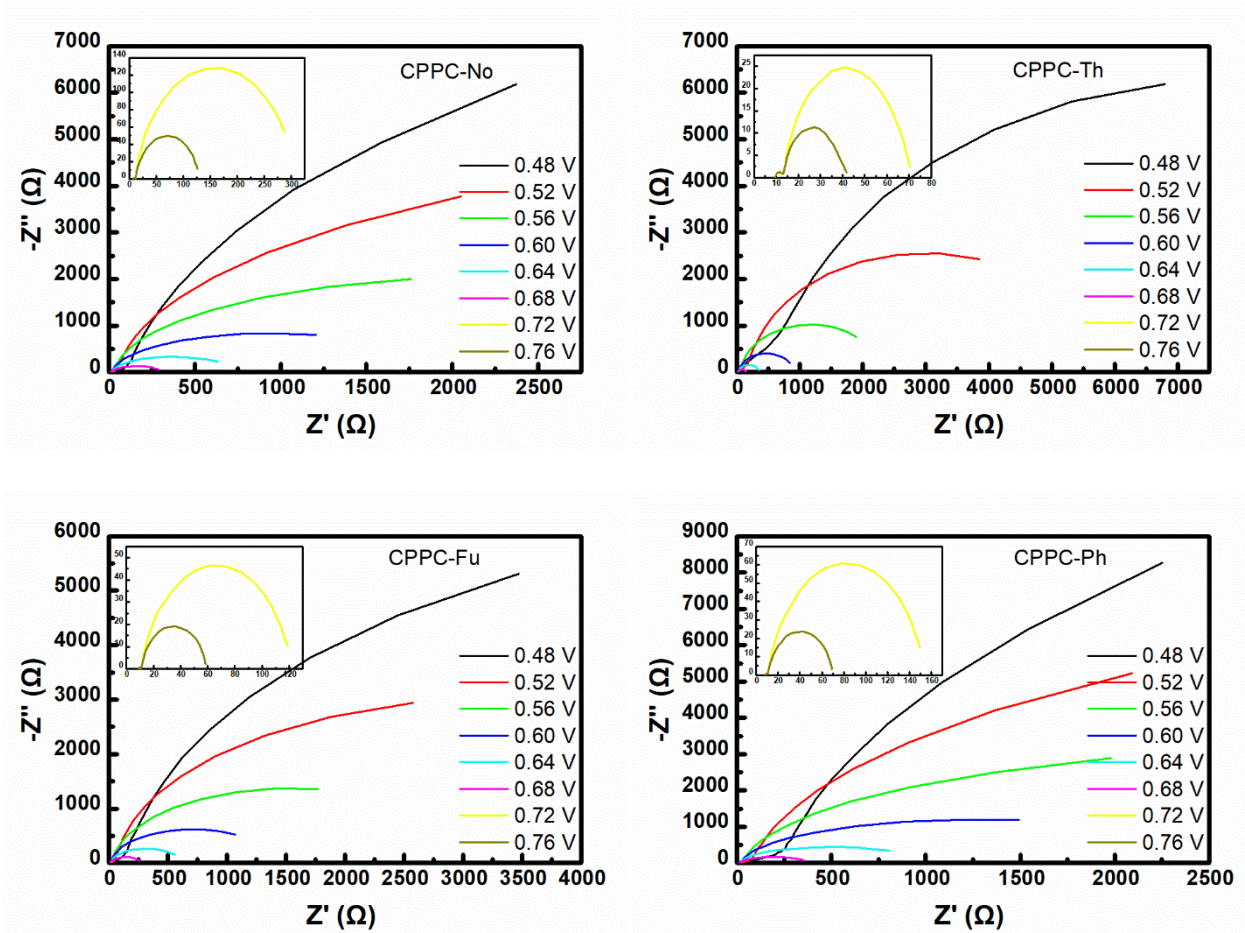


Fig. S7. (a) Charge transport lifetime and (b) charge recombination lifetime of the DSSC devices based on CPPC dyes.



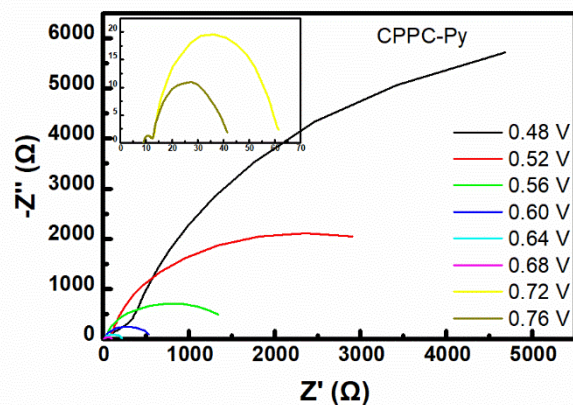


Fig. S8. Nyquist plots of the DSSC devices based on CPPC dyes.

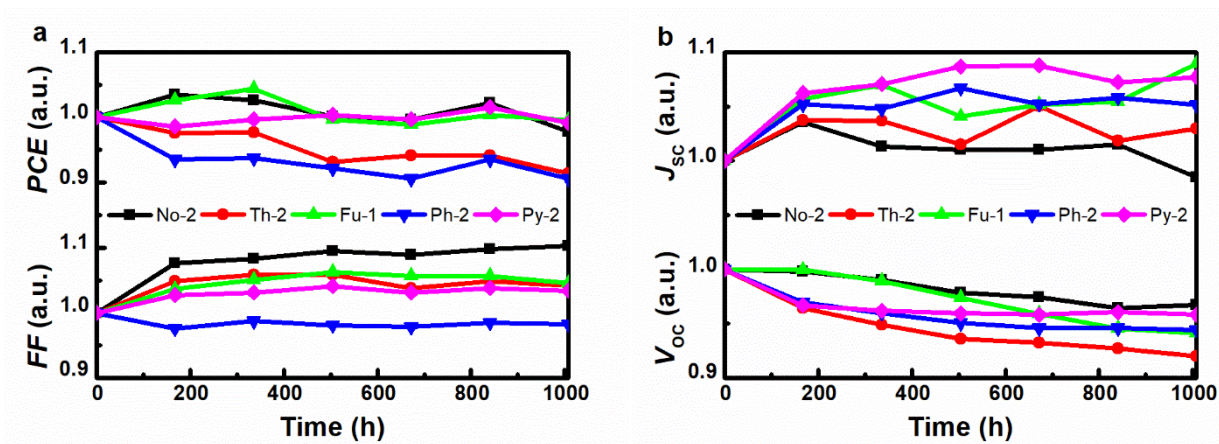


Fig. S9. Time dependence of the (a) PCE , FF and (b) J_{sc} , V_{oc} of the DSSCs based on CPPC dyes obtained over a period of 1000 h in ambient air at room temperature.

Synthesis

5-(7-(3-(9H-carbazol-9-yl)phenyl)-10-hexyl-10H-phenothiazin-3-yl)thiophene-2-carbaldehyde (3)

A mixture of compound **2** (602 mg, 1 mmol), (5-formylthiophen-2-yl)boronic acid (187 mg, 1.2 mmol), $\text{Pd}(\text{PPh}_3)_4$ (116 mg, 0.1 mmol) and tetrabutylammonium bromide (TBAB 96.6 mg, 0.3 mmol) in K_2CO_3 aqueous solution (2.5 ml, 1 M) and tetrahydrofuran (THF, 15 mL) was stirred and heated at 85 °C under a nitrogen atmosphere for 18 h. Water was added to quench the reaction afterwards. The crude product was extracted with DCM and saltwater three times and dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure on a rotary evaporator, and the crude product was purified by column chromatography using petroleum ether/dichloromethane (PE/DCM,

2:1) as the eluent to give compound **3** as a yellow solid in a yield of 34% (216 mg). ¹H NMR (400 MHz, CDCl₃): δ 9.84 (s, 1H), 8.16 (d, *J* = 7.7 Hz, 2H), 7.72 (s, 1H), 7.68 (d, *J* = 4.0 Hz, 1H), 7.62 (s, 1H), 7.51 (d, *J* = 6.7 Hz, 1H), 7.46-7.37 (m, 8H), 7.33-7.25 (m, 3H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 1H), 3.86 (t, *J* = 6.9 Hz, 2H), 1.82 (p, *J* = 7.9 Hz, 2H), 1.48-1.41 (m, 2H), 1.31 (d, *J* = 3.6 Hz, 4H), 0.88 (t, *J* = 6.9 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 181.3, 148.1, 144.8, 143.8, 142.4, 141.1, 140.0, 138.2, 137.1, 130.8, 129.8, 129.3, 127.0, 126.6, 124.7, 123.4, 122.7, 121.4, 120.2, 119.8, 119.1, 118.5, 109.4, 48.7, 31.5, 27.0, 22.7, 14.1. MALDI-TOF (*m/z*): Anal. Calcd. for C₄₁H₃₄N₂O₂S: 634.2113, Found: 634.2110.

5-(7-(3-(9H-carbazol-9-yl)phenyl)-10-hexyl-10H-phenothiazin-3-yl)furan-2-carbaldehyde (4)

A mixture of compound **2** (602 mg, 1 mmol), (5-formylfuran-2-yl)boronic acid (168 mg, 1.2 mmol), Pd(PPh₃)₄ (116 mg, 0.1 mmol) and TBAB (96.6 mg, 0.3 mmol) in K₂CO₃ aqueous solution (2.5 ml, 1 M) and THF (15 mL) was stirred and heated at 85 °C under a nitrogen atmosphere for 18 h. Water was added to quench the reaction afterwards. The crude product was extracted with DCM and saltwater three times and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure on a rotary evaporator, and the crude product was purified by column chromatography using PE/DCM (2:1) as the eluent to give compound **4** as a yellow solid in a yield of 80% (495 mg). ¹H NMR (400 MHz, CDCl₃): δ 9.60 (s, 1H), 8.17 (d, *J* = 7.6 Hz, 2H), 7.73 (s, 1H), 7.68-7.59 (m, 3H), 7.57-7.50 (m, 2H), 7.49-7.38 (m, 6H), 7.31 (t, *J* = 5.9 Hz, 3H), 6.91 (dd, *J* = 18.8, 8.8 Hz, 2H), 6.71 (d, *J* = 3.7 Hz, 1H), 3.96-3.84 (m, 2H), 1.88-1.79 (m, 2H), 1.49-1.44 (m, 2H), 1.32 (dd, *J* = 6.5, 3.7 Hz, 4H), 0.88 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 178.3, 159.8, 153.2, 142.4, 143.0, 139.7, 137.1, 131.8, 130.4, 127.3, 126.6, 122.7, 120.4, 121.3, 119.8, 119.2, 118.7, 116.0, 110.0, 109.2, 48.6, 27.3, 27.0, 22.7, 14.0. MALDI-TOF (*m/z*): Anal. Calcd. for C₄₁H₃₄N₂O₂S: 618.2341, Found: 618.2338.

3-(3-(9H-carbazol-9-yl)phenyl)-10-hexyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine (5)

A mixture of compound **2** (602 mg, 1 mmol), bis(pinacolato)diboron (506 mg, 2 mmol), KOAc (294 mg, 3 mmol) and Pd(dppf)Cl₂ (37 mg, 0.05 mmol) in 1,4-dioxane (10 mL) was stirred and heated

at 110 °C under a nitrogen atmosphere for 12 h. Water was added to quench the reaction afterwards. The crude product was extracted with DCM and saltwater three times and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure on a rotary evaporator, and the crude product was purified by column chromatography using PE/ethyl acetate (EA, 40:1) as the eluent to give compound **5** as a red solid in a yield of 88% (572 mg). ¹H NMR (400 MHz, CD₂Cl₂): δ 8.08 (dd, *J* = 7.8, 2.9 Hz, 2H), 7.67 (d, *J* = 5.2 Hz, 1H), 7.59 (dd, *J* = 4.7, 2.7 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.43-7.27 (m, 7H), 7.25-7.17 (m, 2H), 6.91-6.74 (m, 2H), 3.80 (d, *J* = 20.5 Hz, 2H), 3.64-3.51 (m, 2H), 1.79-1.64 (m, 2H), 1.41-1.30 (m, 2H), 1.22 (d, *J* = 2.0 Hz, 14H), 0.79 (dt, *J* = 8.7, 4.4 Hz, 3H). ¹³C NMR (101 MHz, (CD₃)₂SO): δ 147.5, 144.3, 141.3, 140.6, 140.6, 138.0, 134.8, 134.1, 133.4, 131.2, 126.8, 125.8, 124.6, 124.5, 123.2, 123.2, 122.8, 121.0, 120.5, 120.5, 116.7, 115.7, 110.2, 84.0, 84.0, 47.0, 31.3, 31.3, 26.6, 26.2, 26.2, 25.1, 25.1, 22.5, 22.5, 14.3, 14.3. HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd. for C₄₂H₄₄BN₂O₂S⁺: 651.3217; Found: 651.3224.

6-(7-(3-(9H-carbazol-9-yl)phenyl)-10-hexyl-10H-phenothiazin-3-yl)nicotinaldehyde (6)

A mixture of compound **5** (650 mg, 1 mmol), 2-bromo-5-formylpyridine (279 mg, 1.5 mmol), Pd(PPh₃)₄ (116 mg, 0.1 mmol) and TBAB (96.6 mg, 0.3 mmol) in K₂CO₃ aqueous solution (2.5 ml, 1 M) and THF (15 mL) was stirred and heated at 85 °C under a nitrogen atmosphere for 18 h. Water was added to quench the reaction afterwards. The crude product was extracted with DCM and saltwater three times and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure on a rotary evaporator, and the crude product was purified by column chromatography using PE/DCM (1:1) as the eluent to give compound **6** as a red solid in a yield of 85% (534 mg). ¹H NMR (400 MHz, (CD₃)₂SO): δ 10.10 (d, *J* = 1.5 Hz, 1H), 9.10 (d, *J* = 4.0 Hz, 1H), 8.31-8.23 (m, 3H), 8.18-8.14 (m, 1H), 8.10-8.05 (m, 1H), 8.01-7.98 (m, 1H), 7.90 (d, *J* = 5.2 Hz, 1H), 7.86-7.81 (m, 1H), 7.78-7.72 (m, 1H), 7.67-7.56 (m, 3H), 7.49-7.42 (m, 4H), 7.35-7.28 (m, 2H), 7.21-7.13 (m, 2H), 3.98 (dd, *J* = 17.4, 9.5 Hz, 2H), 1.79-1.71 (m, 2H), 1.44 (d, *J* = 21.2 Hz, 2H), 1.27-1.22 (m, 4H), 0.84 (t, *J* = 4.4 Hz, 3H). ¹³C NMR (101 MHz, (CD₃)₂SO): δ 192.1, 159.8, 152.4, 146.4, 143.9, 141.4, 140.6, 138.4, 137.4, 134.2, 132.2, 131.1, 130.4, 129.9, 127.4, 126.8, 126.1, 125.7, 124.5, 124.0, 123.2, 121.0,

120.5, 119.9, 117.0, 116.1, 110.1, 31.3, 26.3, 22.5, 14.3. HRMS (ESI/QTOF) m/z: [M + H]⁺ Calcd. for C₄₂H₃₆N₃OS⁺: 630.2579; Found: 630.2579.

3-(7-(3-(9H-carbazol-9-yl)phenyl)-10-hexyl-10H-phenothiazin-3-yl)-2-cyanoacrylic acid (CPPC-No)

A mixture of compound **1** (552 mg, 1 mmol), cyanoacetic acid (170 mg, 2 mmol) and NH₄OAc (77 mg, 1 mmol) in CH₃COOH (10 mL) was stirred and heated at 90 °C under a nitrogen atmosphere for 24 h. Water was added to quench the reaction afterwards. The crude product was extracted with DCM and saltwater three times and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure on a rotary evaporator, and the crude product was purified by column chromatography using methanol (MeOH)/DCM (1:20) as the eluent to give **CPPC-No** as a crimson solid in a yield of 95% (588 mg). ¹H NMR (400 MHz, CDCl₃): δ 8.16 (d, *J* = 7.7 Hz, 2H), 8.08 (s, 1H), 7.93 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.73 (d, *J* = 1.7 Hz, 1H), 7.64 (tdd, *J* = 7.9, 5.8, 2.4 Hz, 3H), 7.55-7.51 (m, 1H), 7.48-7.40 (m, 6H), 7.36 (d, *J* = 2.1 Hz, 1H), 7.30 (ddd, *J* = 8.0, 6.7, 1.4 Hz, 2H), 6.91 (dd, *J* = 21.9, 8.7 Hz, 2H), 3.93-3.87 (m, 2H), 1.84 (dt, *J* = 14.8, 7.5 Hz, 2H), 1.46 (s, 2H), 1.37-1.30 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 168.1, 168.1, 154.4, 149.6, 142.3, 141.3, 140.8, 138.3, 135.7, 132.0, 130.4, 126.3, 126.1, 125.8, 125.4, 125.4, 124.9, 124.0, 123.9, 123.8, 123.7, 123.5, 120.4, 120.1, 116.1, 116.0, 114.9, 109.8, 97.7, 48.2, 31.4, 26.6, 26.5, 22.6, 14.1, 14.0. HRMS (ESI/QTOF) m/z: [M - H]⁻ Calcd. for C₄₀H₃₂N₃O₂S⁻: 618.2215; Found: 618.2215.

3-(5-(7-(3-(9H-carbazol-9-yl)phenyl)-10-hexyl-10H-phenothiazin-3-yl)thiophen-2-yl)-2-cyanoacrylic acid (CPPC-Th)

A mixture of compound **3** (634 mg, 1 mmol), cyanoacetic acid (170 mg, 2 mmol) and NH₄OAc (77 mg, 1 mmol) in CH₃COOH (10 mL) was stirred and heated at 90 °C under a nitrogen atmosphere for 24 h. Water was added to quench the reaction afterwards. The crude product was extracted with DCM and saltwater three times and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure on a rotary evaporator, and the crude product was purified by column chromatography using MeOH/DCM (1:20) as the eluent to give **CPPC-Th** as a crimson solid in a

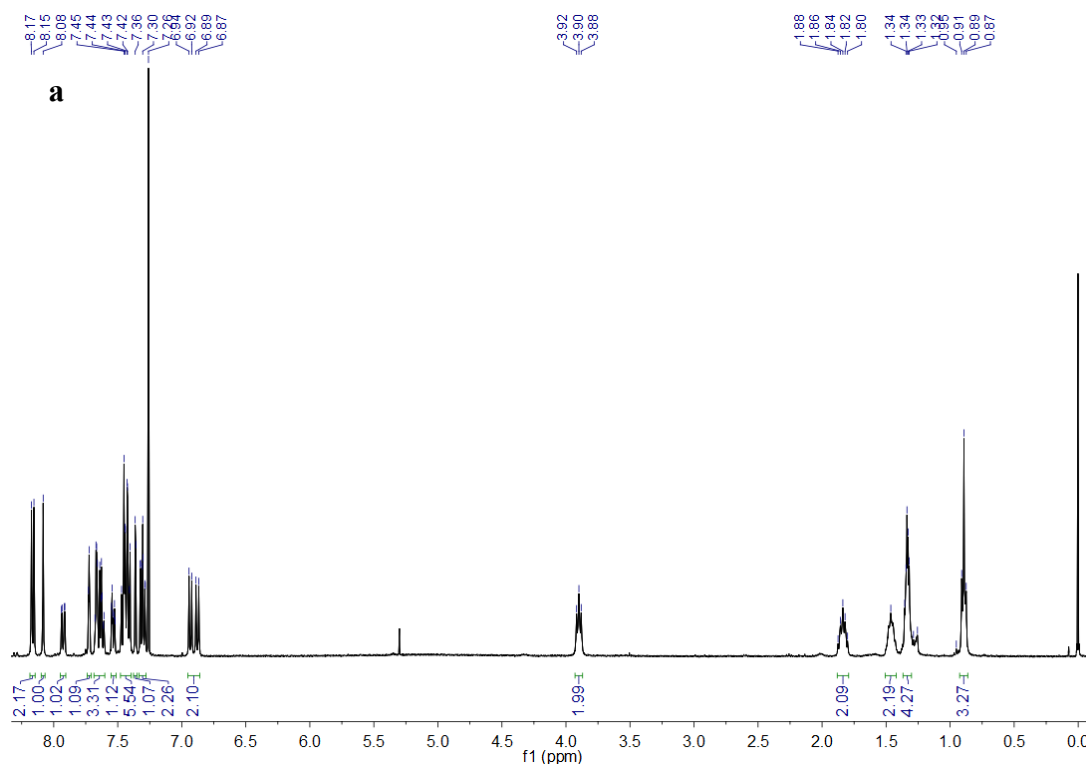
yield of 93% (650 mg). ¹H NMR (400 MHz, (CD₃)₂SO): δ 8.46 (s, 1H), 8.26 (d, *J* = 7.8 Hz, 2H), 7.97 (d, *J* = 4.1 Hz, 1H), 7.87 (s, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.76-7.67 (m, 2H), 7.64-7.54 (m, 6H), 7.48-7.40 (m, 4H), 7.30 (ddd, *J* = 7.9, 5.3, 2.7 Hz, 2H), 7.10 (t, *J* = 9.5 Hz, 2H), 3.92 (t, *J* = 7.2 Hz, 2H), 1.45-1.35 (m, 2H), 1.29-1.19 (m, 6H), 0.82 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, (CD₃)₂SO): δ 164.1, 152.0, 145.8, 143.9, 141.3, 140.6, 138.0, 134.5, 134.2, 131.2, 127.2, 126.8, 126.4, 125.9, 125.8, 124.8, 124.7, 124.6, 124.5, 123.7, 123.3, 121.0, 120.5, 117.4, 116.8, 116.7, 110.2, 47.2, 31.6, 31.3, 30.3, 29.50, 26.6, 26.3, 22.5, 14.3. HRMS (ESI/QTOF) *m/z*: [M - H⁺]⁻ Calcd. for C₄₄H₃₄N₃O₂S₂⁻: 700.2092; Found: 700.2092.

3-(5-(7-(3-(9H-carbazol-9-yl)phenyl)-10-hexyl-10H-phenothiazin-3-yl)furan-2-yl)-2-cyanoacrylic acid (CPPC-Fu)

A mixture of compound **4** (618 mg, 1 mmol), cyanoacetic acid (170 mg, 2 mmol) and NH₄OAc (77 mg, 1 mmol) in CH₃COOH (10 mL) was stirred and heated at 90 °C under a nitrogen atmosphere for 24 h. Water was added to quench the reaction afterwards. The crude product was extracted with DCM and saltwater three times and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure on a rotary evaporator, and the crude product was purified by column chromatography using MeOH/DCM (1:15) as the eluent to give **CPFC-Fu** as a crimson solid in a yield of 91% (620 mg). ¹H NMR (400 MHz, (CD₃)₂SO): δ 8.26 (d, *J* = 7.8 Hz, 2H), 8.02 (s, 1H), 7.89 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.78-7.67 (m, 3H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.57 (d, *J* = 9.5 Hz, 1H), 7.51 (d, *J* = 4.0 Hz, 1H), 7.49-7.38 (m, 4H), 7.38-7.24 (m, 4H), 7.15 (dd, *J* = 16.3, 9.5 Hz, 2H), 4.06-3.87 (m, 2H), 1.79-1.62 (m, 2H), 1.34-1.24 (m, 6H), 0.82 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, (CD₃)₂SO): δ 164.5, 158.8, 147.7, 146.0, 143.9, 141.3, 140.6, 138.0, 137.9, 134.3, 131.2, 127.5, 126.8, 125.9, 125.8, 125.3, 124.6, 124.2, 123.9, 123.6, 123.3, 123.3, 121.0, 120.5, 117.2, 116.9, 116.6, 110.2, 109.6, 96.8, 47.3, 32.0, 31.8, 31.3, 29.9, 29.5, 29.2, 26.8, 26.6, 26.2, 22.5, 14.4, 14.3. HRMS (ESI/QTOF) *m/z*: [M - H⁺]⁻ Calcd. for C₄₄H₃₄N₃O₃S⁻: 684.2321; Found: 684.2321.

3-(6-(7-(3-(9H-carbazol-9-yl)phenyl)-10-hexyl-10H-phenothiazin-3-yl)pyridin-3-yl)-2-cyanoacrylic acid (CPPC-Py)

A mixture of compound **6** (629 mg, 1 mmol), cyanoacetic acid (170 mg, 2 mmol) and NH₄OAc (77 mg, 1 mmol) in CH₃COOH (15 mL) was stirred and heated at 85 °C under a nitrogen atmosphere for 20 h. Water was added to quench the reaction afterwards. The crude product was extracted with DCM and saltwater three times and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure on a rotary evaporator, and the crude product was purified by column chromatography using MeOH/DCM (1:20) as the eluent to give **CPFC-Py** as a red solid in a yield of 86% (599 mg). ¹H NMR (400 MHz, (CD₃)₂SO): δ 8.94 (d, *J* = 4.5 Hz, 1H), 8.46-8.37 (m, 1H), 8.28 (dd, *J* = 7.8, 2.7 Hz, 2H), 8.11-8.06 (m, 1H), 8.05-7.97 (m, 2H), 7.97-7.93 (m, 1H), 7.90 (d, *J* = 5.3 Hz, 1H), 7.87-7.80 (m, 1H), 7.78-7.70 (m, 1H), 7.68-7.54 (m, 3H), 7.51-7.39 (m, 4H), 7.36-7.27 (m, 2H), 7.21-7.08 (m, 2H), 4.02-3.92 (m, 2H), 1.74 (d, *J* = 14.6 Hz, 2H), 1.42 (s, 2H), 1.33-1.20 (m, 4H), 0.90-0.76 (m, 3H). ¹³C NMR (101 MHz, (CD₃)₂SO): δ 156.5, 151.7, 146.2, 144.1, 141.3, 140.6, 138.0, 136.5, 134.1, 132.3, 131.2, 126.8, 125.8, 124.6, 124.5, 124.0, 123.8, 123.2, 121.0, 120.5, 119.6, 116.3, 110.2, 31.3, 26.6, 26.3, 22.5, 14.3. HRMS (ESI/QTOF) *m/z*: [M - H⁺]⁻ Calcd. for C₄₅H₃₅N₄O₂S⁻: 695.2481; Found 695.2480.



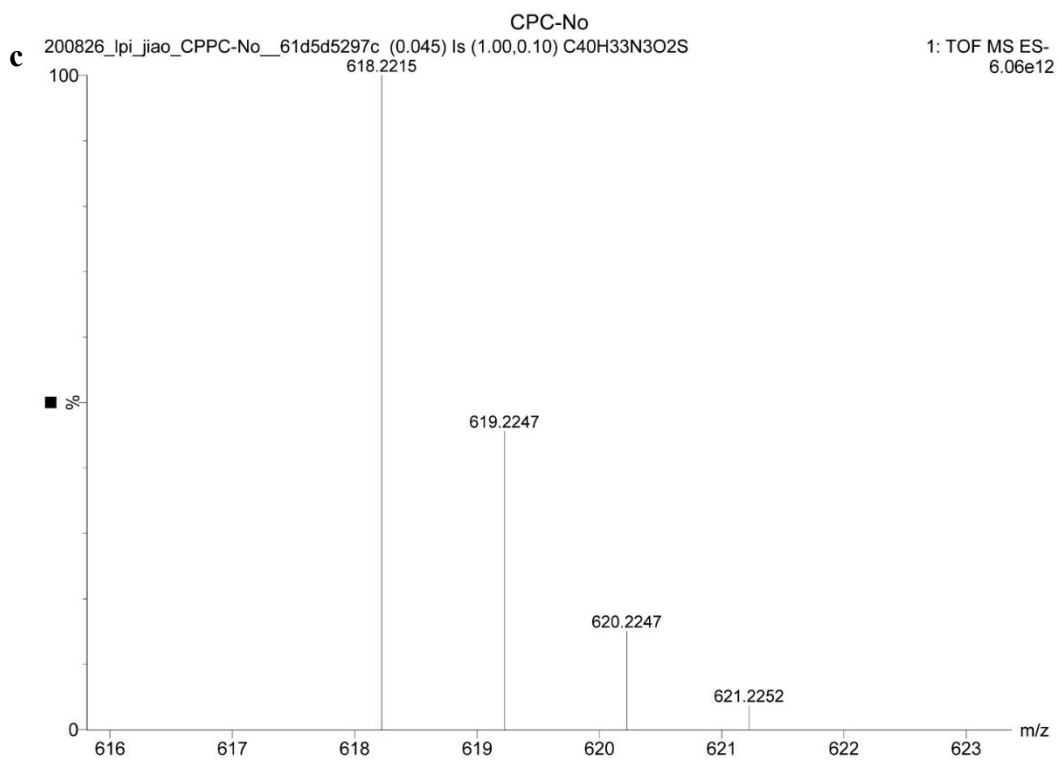
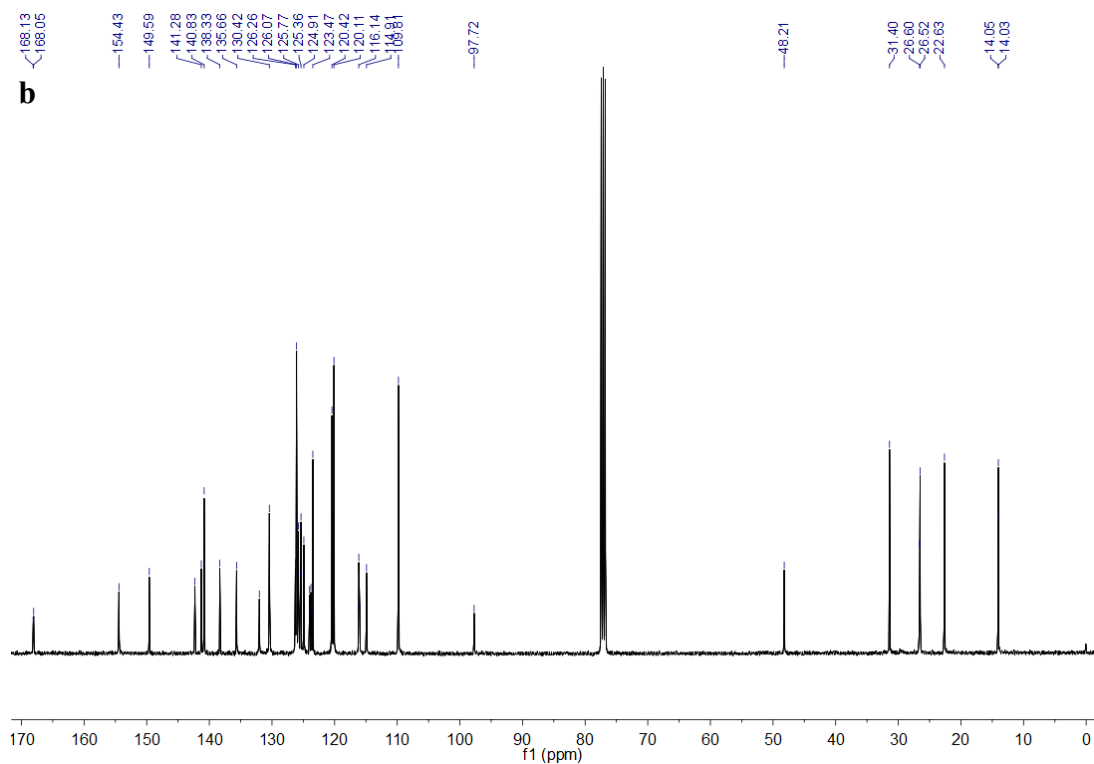
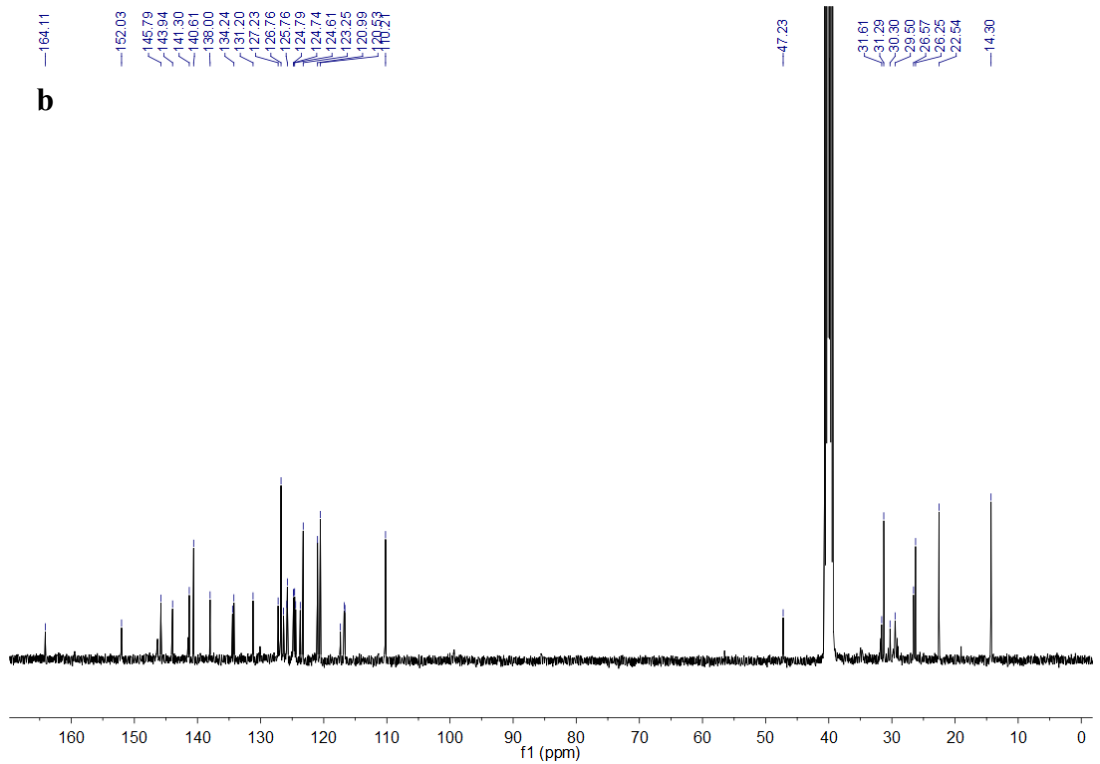
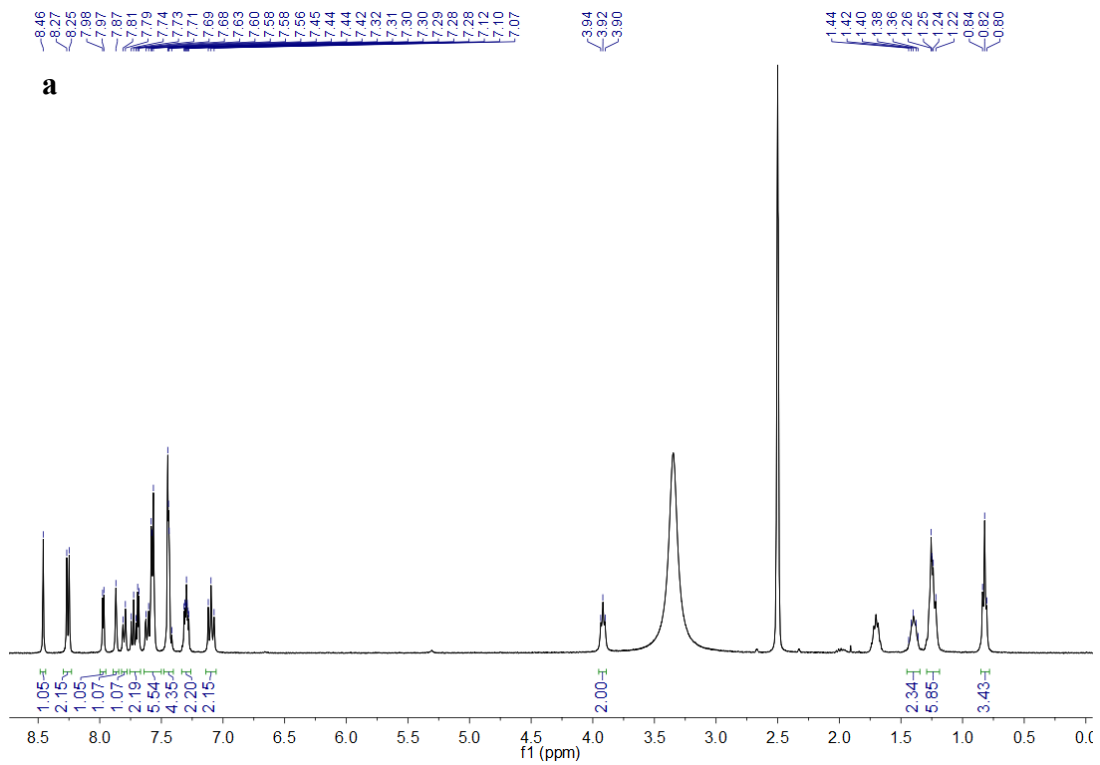


Fig. S10. (a) ^1H NMR in CDCl_3 , (b) ^{13}C NMR in CDCl_3 and (c) HRMS of CPC-No.



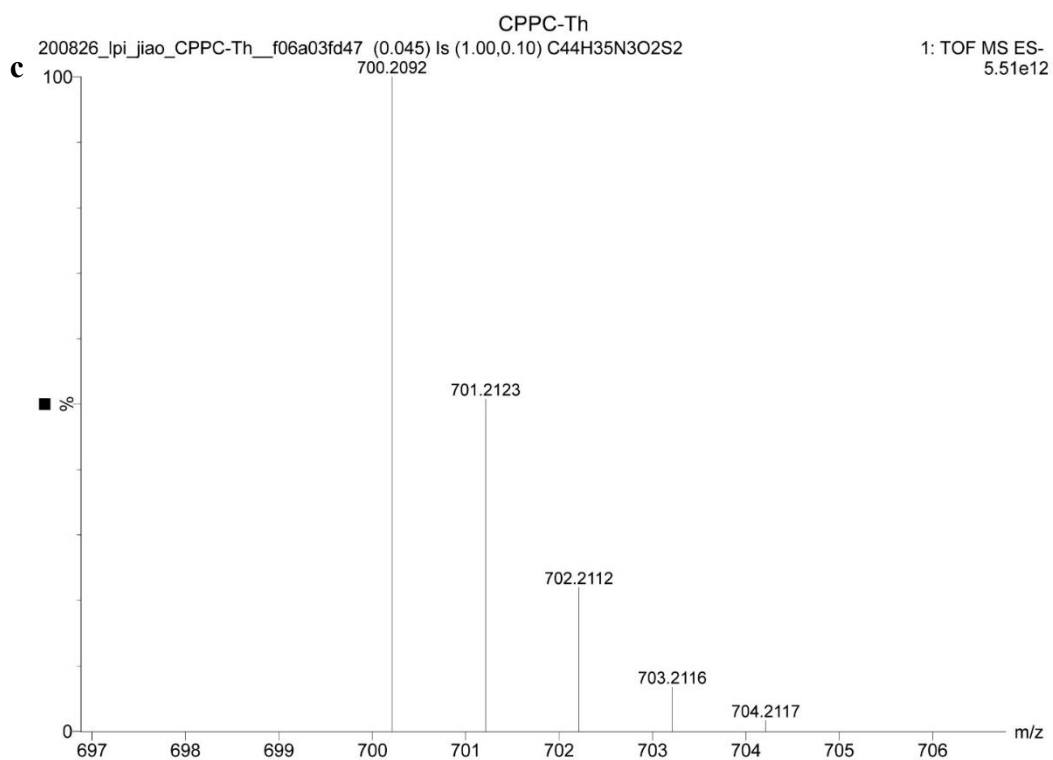
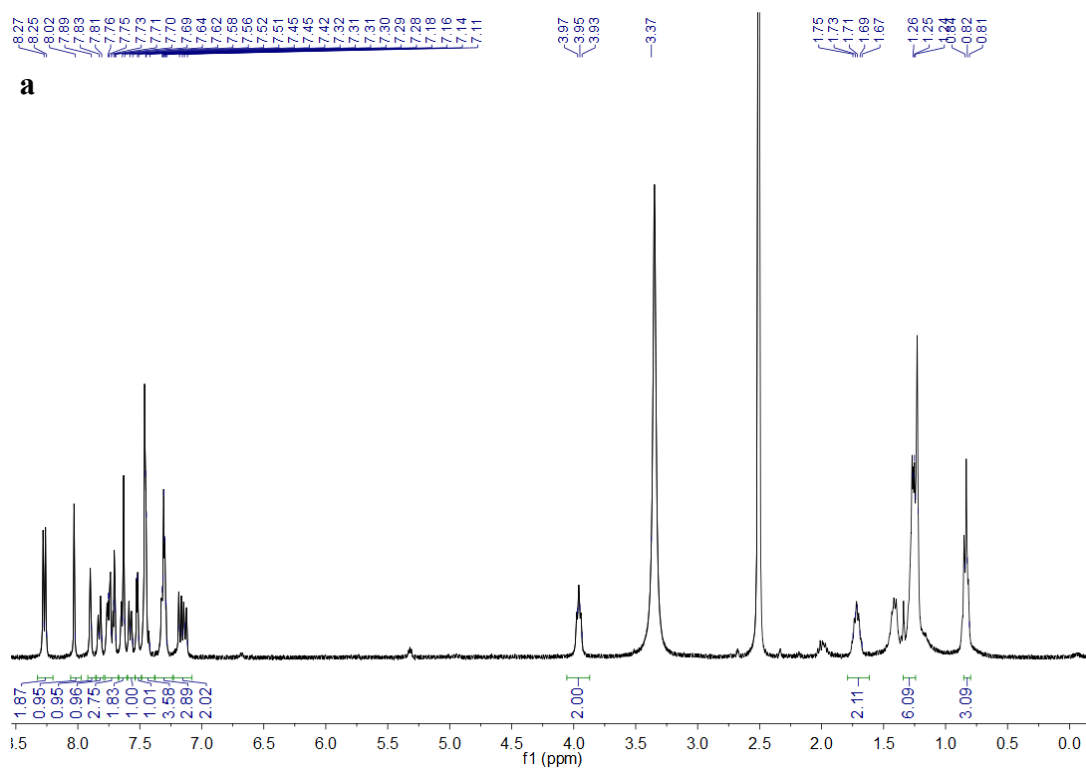


Fig. S11. (a) ^1H NMR in $(\text{CD}_3)_2\text{SO}$, (b) ^{13}C NMR in $(\text{CD}_3)_2\text{SO}$ and (c) HRMS of CPPC-Th.



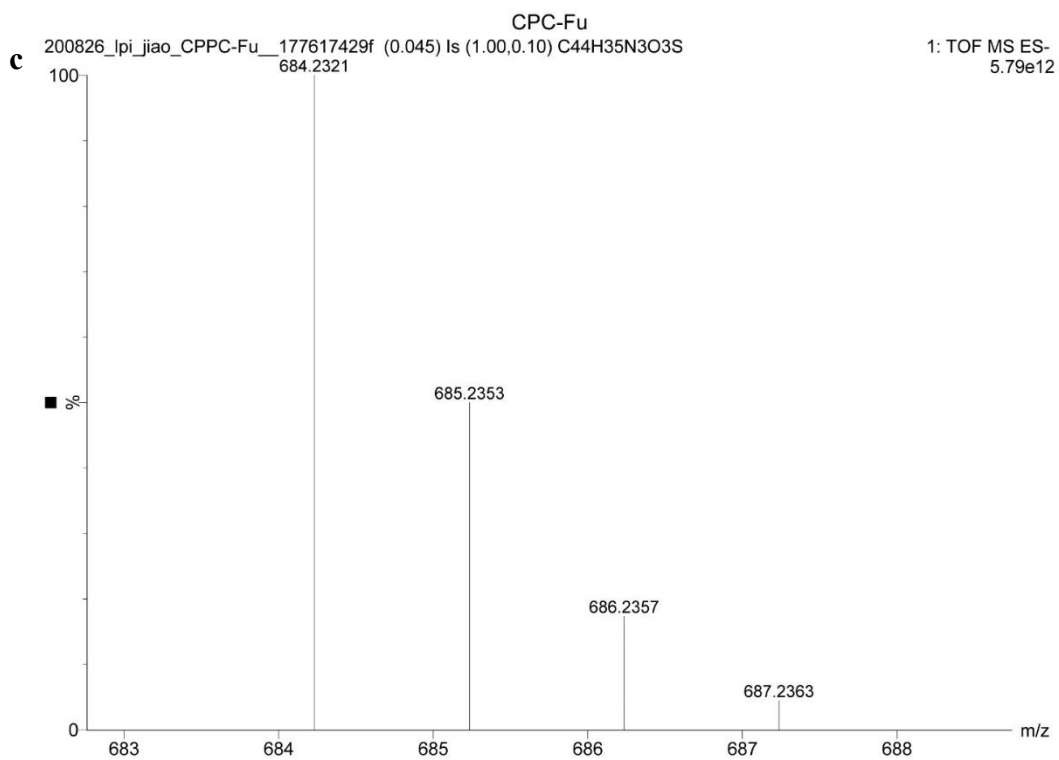
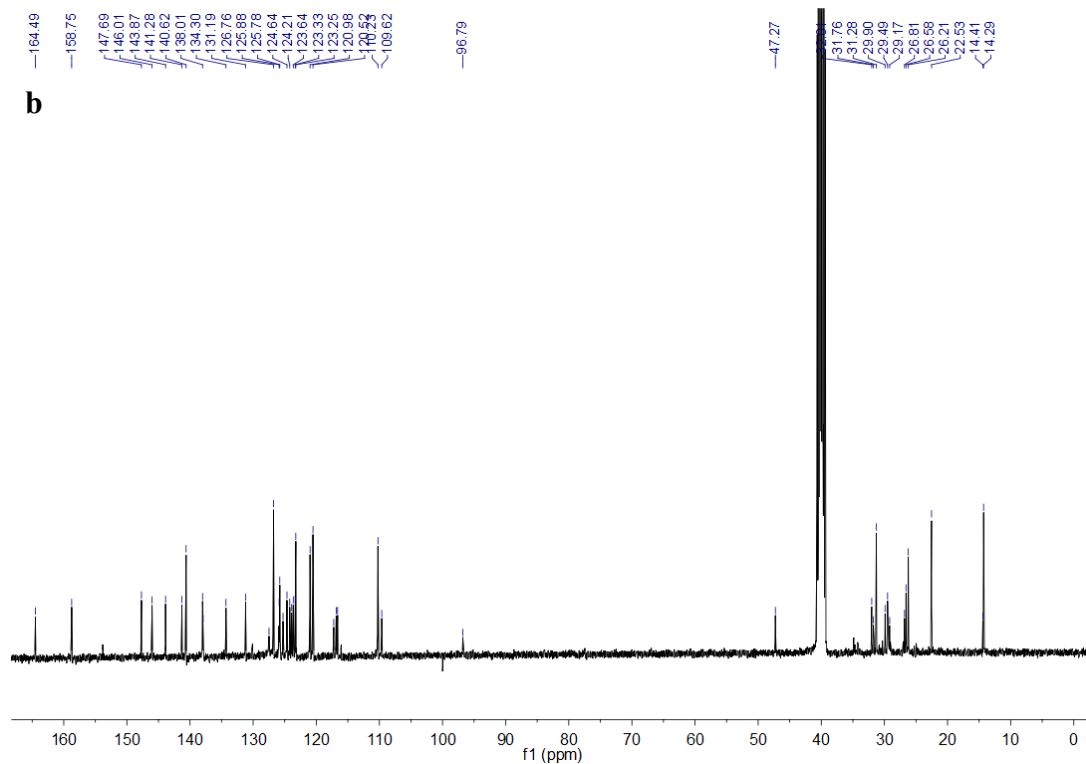
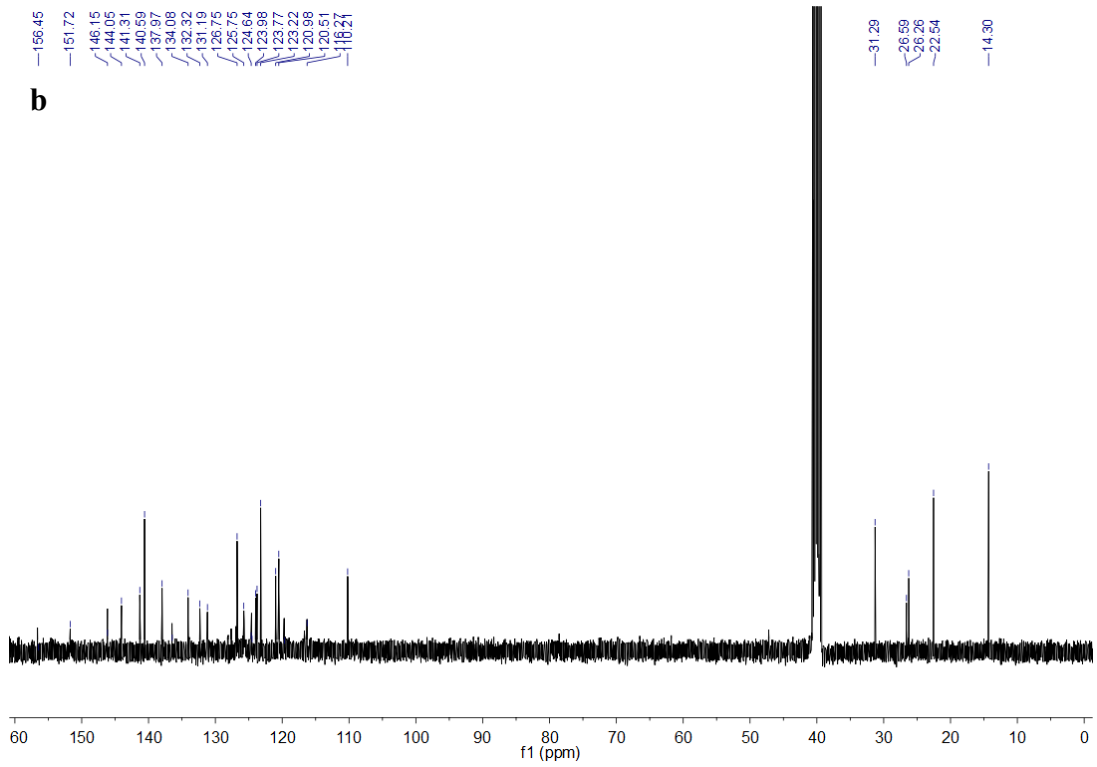
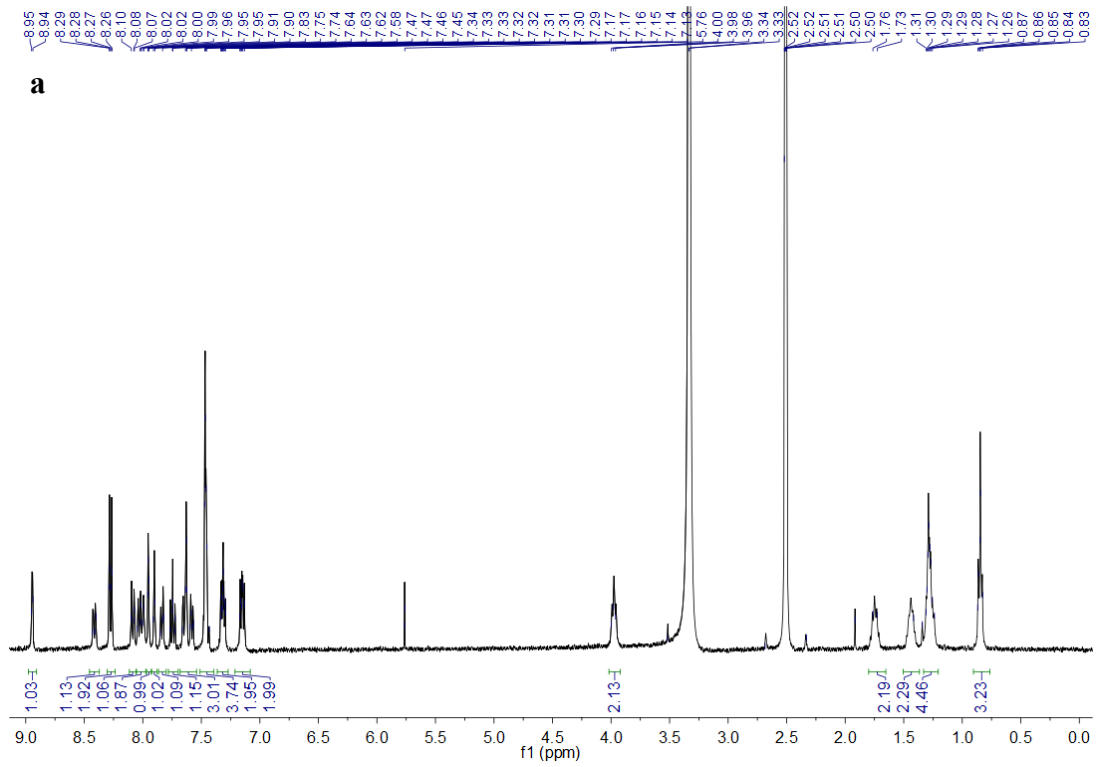


Fig. S12. (a) ^1H NMR in $(\text{CD}_3)_2\text{SO}$, (b) ^{13}C NMR in $(\text{CD}_3)_2\text{SO}$ and (c) HRMS of **CPPC-Fu**.



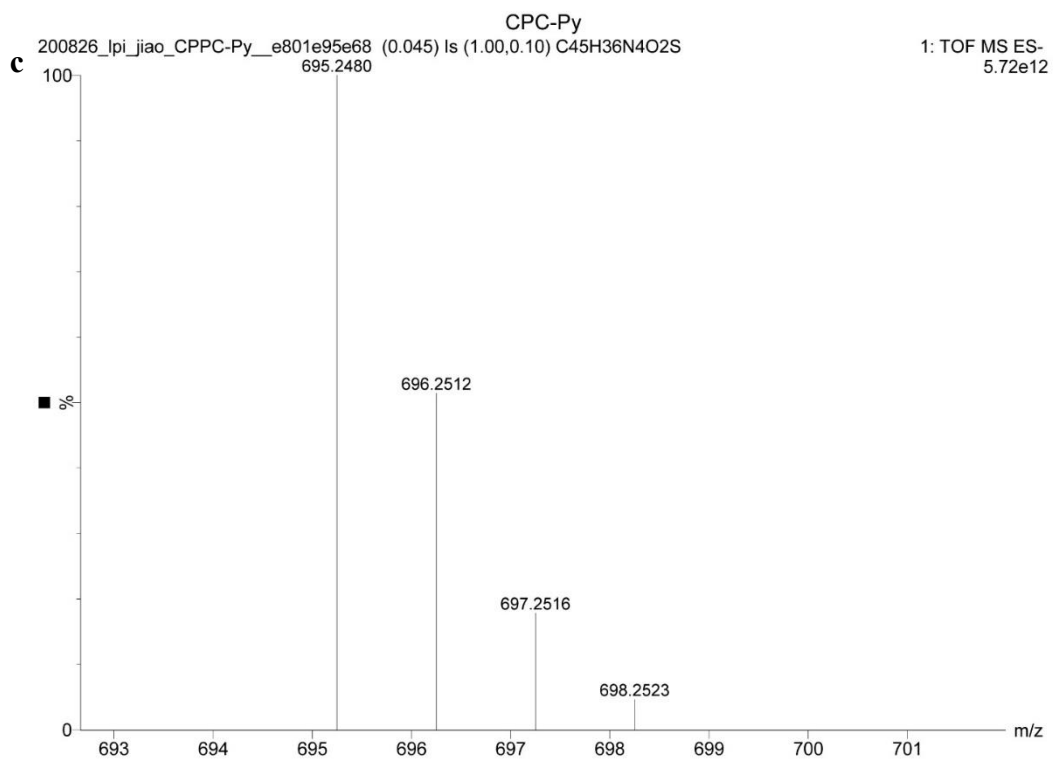


Fig. S13. (a) ^1H NMR in $(\text{CD}_3)_2\text{SO}$, (b) ^{13}C NMR in $(\text{CD}_3)_2\text{SO}$ and (c) HRMS of CPPC-Py.