Electronic Supplementary Information

Peptide linked perylenebisimide and ferrocene dicarboxylic acid conjugates with tuneable optoelectronic properties

Biswanath Hansda, Soumyajit Hazra, Niladri Hazra, Purnadas Ghosh, and Arindam Banerjee*

School of Biological Sciences, Indian Association for the Cultivation of Science, 2A & 2B Raja S. C. Mullick Road, Jadavpur, Kolkata 700032, India

Email: bcab@iacs.res.in

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Synthesis of B_2KFO: Boc-L-lysine-OH (6.92 g, 30 mmol) was dissolved in minimum amount N,N-dimethyl formamide (DMF, 20 ml) and cooled to 0 °C. H_2N-Phe-OMe (5.37 g, 30 mmol) was obtained from its hydrochloride salt by treated with Et_3N in ethyl acetate and DMF solution and subsequently filtering to remove the precipitate. The filtrate was added to the cooled solution followed by the subsequent addition of hydroxybenzotriazole (HOBt, 4.05 g, 30 mmol) and N,N-dicyclohexylcarbodiimide (DCC, 6.6 g, 32 mmol).The reaction mixture was stirred for 24 h at room temperature and filtered for separation of N,N-dicyclohexyl urea (DCU). The reaction mixture was diluted with ethyl acetate and washed with 1(N) HCl (3 × 40 ml), saturated brine (2 × 40 ml), saturated sodium carbonate solution (3 × 40 ml) and again saturated brine (2 × 40 ml). The ethyl acetate layer was dried over Na_2SO_4 and the solvent was evaporated. The yellowish product obtained was purified by silica gel column chromatography using the mixture of petroleum ether and ethyl acetate (5:1) as eluent and the white pure product Boc_2-K-F-OMe (B_2KFO) was obtained. Yield: 13.18 g (26 mmol, 86.66%).

^{1}H NMR:- δ_H (400 MHz, $CDCl_3$) 7.34 – 7.26 (2 H, m), 7.24 (3 H, dd, *J* 12.9, 6.8), 7.14 (1 H, s), 7.13 – 7.04 (2 H, m), 6.66 (1 H, d, *J* 7.7), 5.16 (1 H, d, *J* 7.7), 4.88 – 4.80 (1 H, m), 4.70 (1 H, s), 4.03 (1 H, s), 3.69 (3 H, s), 3.20 (4 H, s), 3.13 (1 H, dd, *J* 13.9, 5.8), 3.05 (3 H, dt, *J* 12.2, 6.0), 2.94 (1 H, s), 2.86 (1 H, s), 2.81 (1 H, s), 1.78 – 1.70 (1 H, m), 1.62 – 1.53 (2 H, m), 1.51 (2 H, s), 1.47 (0 H, d, *J* 5.4), 1.45 (2 H, s), 1.29 (2 H, dd, *J* 15.5, 8.3), 1.23 (3 H, s).

^{13}C NMR: - δ_C (101 MHz, $CDCl_3$) 171.88, 171.81, 156.29, 135.92, 129.42, 128.76, 127.31, 53.28, 52.48, 38.10, 34.12, 32.10, 29.79, 28.60, 28.46, 22.60.

HRMS (m/z): Calculated for $C_{26}H_{41}N_3O_7$: 507.63 [M], Found: 530.31 $[M+Na]^+$

Synthesis of B_2KF-OH: In a round bottomed flask 10.14 g (20 mmol) of Boc_2-K-F-OMe was dissolved in 120 ml methanol and added 82 ml of 1(N) NaOH solution. The hydrolysis reaction was stirred for 6 hours and monitored by thin layer chromatography (TLC) time to time. After complete hydrolysis, methanol was evaporated in vacuum. The aqueous solution was acidified with 1(N) HCl and extracted with ethyl acetate (4 × 50 ml) which subsequently dried over anhydrous Na_2SO_4. The ethyl acetate was evaporated in rotary evaporator and the white compound (B_2KF-OH) was obtained. Yield: 8.87 g (18 mmol, 90%)

^{1}H NMR:- δ_H (400 MHz, DMSO) 12.69 (1 H, s), 7.87 (1 H, d, *J* 7.9), 7.30 – 7.14 (5 H, m), 6.80 – 6.70 (2 H, m), 4.41 (1 H, td, *J* 8.1, 5.0), 3.84 (1 H, td, *J* 8.7, 4.9), 3.04 (1 H, dd, *J* 13.8, 5.2), 2.96 – 2.85 (1 H, m), 2.89 – 2.78 (2 H, m), 2.52 (2 H, s), 1.47 (2 H, s), 1.36 (14 H, d, *J* 3.0), 1.24 (1 H, d, *J* 5.7), 0.99 (1 H, s).

^{13}C NMR: - δ_C (101 MHz, DMSO) 173.23, 172.48, 156.03, 155.64, 137.87, 129.67, 128.56, 126.83, 78.50, 77.79, 54.86, 53.65, 37.27, 32.14, 29.69, 28.76, 28.66, 23.20.

HRMS (m/z): Calculated for $C_{25}H_{39}N_3O_7$: 493.60 [M], Found: 516.27 $[M+Na]^+$

Synthesis of B_2KFC_6-NH_2: B_2KF-OH (18 mmol, 8.87 g) was taken into a round bottom flux treating with N-hydroxysuccinimide (4.8 eqv, 13.39 g) followed by excess N,N'-Dicyclohexylcarbodiimide (DCC) in tetrahydrofuran (THF) in ice-bath condition. The reaction was carried out for 24 h at room temperature. The reaction mixture was filtered and THF was

evaporated in rotary evaporator. Then in a 500 ml round bottomed flask, the ester formed was dissolved in 220ml DCM and added drop wise to a solution of 1, 6-hexanediamine (75 mmol, 8.71 g) in 140 ml DCM for 2 h. The reaction mixture was stirred for 24 hours at room temperature and then it was transferred to a separating funnel. The reaction mixture was washed with water (6 x 350 ml) followed by saturated brine solution (200 ml) and hence the precipitate, formed during the dropwise addition of the ester, disappeared. The organic layer was separated and dried over anhydrous Na_2SO_4. The organic solvent was evaporated in rotary evaporator. The crude compound was purified by Column chromatography initially run by $CHCl_3$: MeOH, 95 : 5 (v/v) as an eluent to remove difunctionalized compound from the crude and subsequently changing the eluent to $CHCl_3$: MeOH : $N(Et)_3$, 90 : 5 : 5 (v/v) to obtain the purified desired compound as a sticky yellowish solid.

Yiels: 7.68 g (13 mmol, 72.22%).

1H NMR:- δ_H (400 MHz, DMSO) 8.25 (1 H, d, *J* 8.4), 8.11 (1 H, t, *J* 5.7), 7.91 – 7.85 (1 H, m), 7.42 (2 H, s), 7.24 (1 H, d, *J* 7.5), 7.23 – 7.12 (4 H, m), 6.98 (1 H, dd, *J* 18.2, 7.3), 6.78 (1 H, t, *J* 5.8), 4.47 – 4.38 (1 H, m), 4.26 (12 H, s), 3.77 (1 H, q, *J* 7.6, 6.1), 3.46 (2 H, p, *J* 7.6, 6.0), 3.16 (1 H, d, *J* 13.9), 3.06 (1 H, dd, *J* 13.5, 6.6), 3.00 – 2.90 (1 H, m), 2.84 (2 H, d, *J* 7.0), 2.45 (2 H, q, *J* 7.1), 1.77 (6 H, s), 1.77 – 1.66 (5 H, m), 1.58 (2 H, d, *J* 12.8), 1.47 (2 H, d, *J* 7.0), 1.40 (4 H, s), 1.37 (16 H, s), 1.35 – 1.19 (16 H, m), 1.07 (3 H, h, *J* 8.8), 0.94 (3 H, t, *J* 7.2). (Modify this proton NMR- exclude some of the protons)

^{13}C NMR:- δ_C (101 MHz, DMSO) 174.04, 172.31, 171.18, 156.04, 155.88, 153.86, 138.25, 129.64, 129.55, 128.41, 128.38, 126.61, 78.53, 77.75, 55.42, 54.98, 54.55, 51.14, 46.07, 41.74, 38.84, 38.25, 32.85, 32.03, 31.58, 29.65, 29.34, 29.26, 28.94, 28.73, 28.61, 26.35, 26.30, 26.19,

25.32, 25.12, 23.87, 23.13, 22.77, 11.94. (Modify this carbon NMR- exclude some of the carbons)

HRMS (m/z): Calculated for $C_{31}H_{53}N_5O_6$: 951.79 [M], Found: 592.36 $[M+H]^+$

Synthesis of PBI-($C_6FKB_2)_2$: Perylene-3, 4, 9, 10-tetracarboxilicbisanhydride (PBI) (1 mmol, 392.32 mg) and B_2KFC_6-NH2 (2.5 mmol, 1.47 g) were mixed in 15 ml dry DMF in a 100 ml RB and stirred for overnight at 140º C. Then the reaction mixture was cooled to room temperature. Cold diethyl ether was added to the mixture and kept in deep fridge for precipitation. The precipitate was filtrate out and confirmed formation of di-Boc protected compound was identified by HRMS data. The crude compound was purified by the coloumn chromatography in silica gel (100–200 mesh) using chloroform/methanol (97:3) as eluents.

Yiels: 0.82 g (0.53 mmol, 53%).

1H NMR:- δ_H (400 MHz, DMSO) 8.49 (1 H, s), 8.26 (1 H, s), 7.93 (1 H, s), 7.24 – 7.19 (3 H, m), 4.48 (1 H, s), 4.11 (1 H, s), 4.01 (1 H, s), 2.97 (2 H, s), 2.34 (1 H, s), 1.65 (1 H, s), 1.35 (1 H, s), 1.27 (6 H, s), 1.16 (1 H, s).

HRMS (m/z): Calculated for $C_{86}H_{110}N_{10}O1_6$: 1539.88 $[M]^+$, Found: 1540.76 $[M+H]^+$, 1562.74 $[M+Na]^+$

Synthesis of PBI-[C_6FK-($NH_2)_2$] (PBI-CFK): PBI-($C_6FKB_2)_2$ (0.53 mmol) was dissolved in 10-mL dichloromethane, and 2 mL trifluroaceticacid was added drop wise to the reaction mixture. The progress of the reaction was monitored by thin layer chromatography (TLC). After 4 h, TFA was removed under vacuum. Then, the reaction mixture was poured into ice cold water and neutralized carefully with 10% NH_3 solution until pH reached at 8. The residue was

extracted with dichloromethane, washed with brine, and dried over Na_2SO_4. After evaporating the solvent, the crude product was purified column chromatography in basic alumina, and pure dark brown compound was obtained.

Yiels: 0.34 g (0.30 mmol, 56.60%).

δ_H (400 MHz, DMSO) 8.61 (3 H, s), 8.33 (3 H, dd, *J* 11.6, 6.2), 8.15 – 8.09 (5 H, m), 8.05 (3 H, s), 7.80 (6 H, s), 7.24 (10 H, tq, *J* 15.1, 7.2), 4.51 (1 H, q, *J* 7.7), 4.03 (4 H, s), 3.75 (2 H, s), 3.20 – 3.10 (3 H, m), 3.04 (1 H, q, *J* 6.8, 5.6), 2.96 (2 H, dd, *J* 14.1, 6.1), 2.86 (1 H, d, *J* 15.5), 2.76 (2 H, t, *J* 9.4), 2.54 (11 H, s), 2.13 (1 H, s), 2.09 (7 H, s), 1.67 (5 H, s), 1.53 (2 H, t, *J* 7.7), 1.35 (19 H, s), 1.29 – 1.14 (4 H, m).

^{13}C NMR:- 170.12, 168.28, 162.49, 137.28, 129.13, 129.08, 128.07, 126.37, 123.86, 122.29, 51.76, 30.61, 28.90, 26.34, 20.85

HRMS (m/z): Calculated for $C_{66}H_{78}N_{10}O_8$: 1139.41 [M], Found: 1161.94 $[M+Na]^+$, 1177.92 $[M+K]^+$

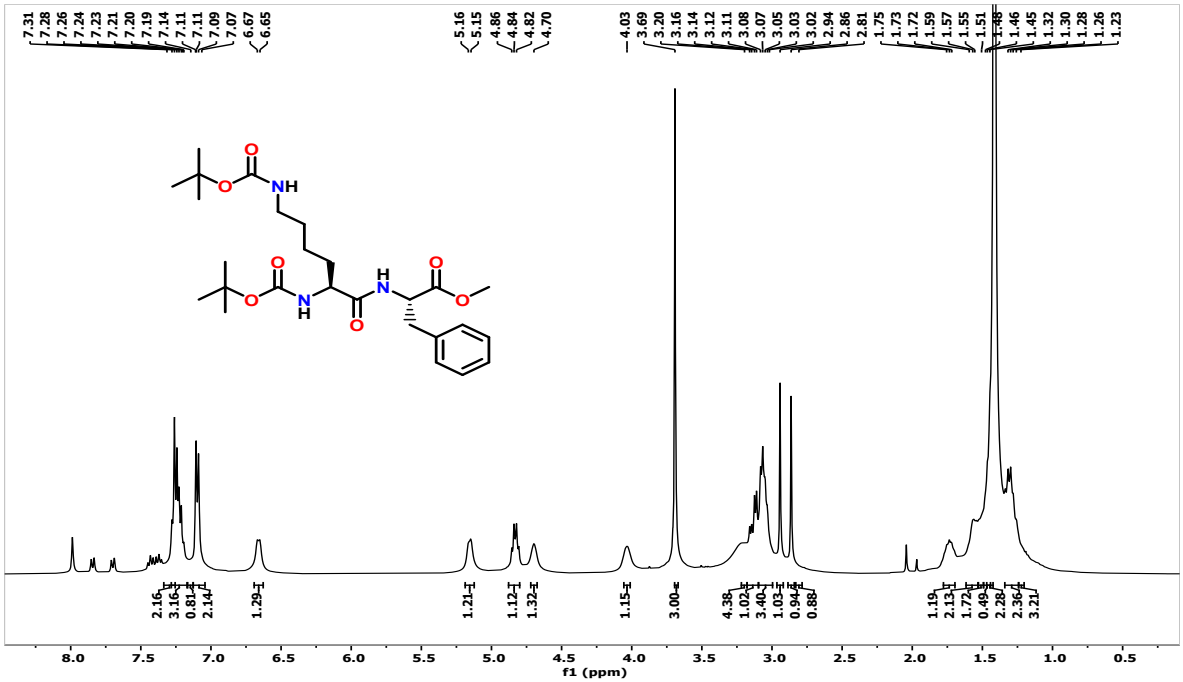

Fig. S1 ^{1}H NMR spectra of B_2KFO

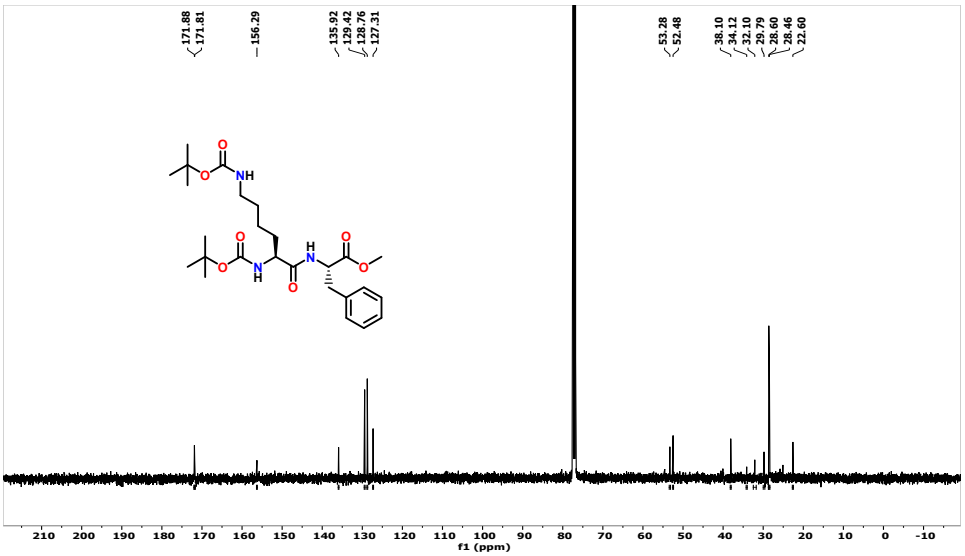

Fig. S2 ^{13}C NMR spectra of B_2KFO

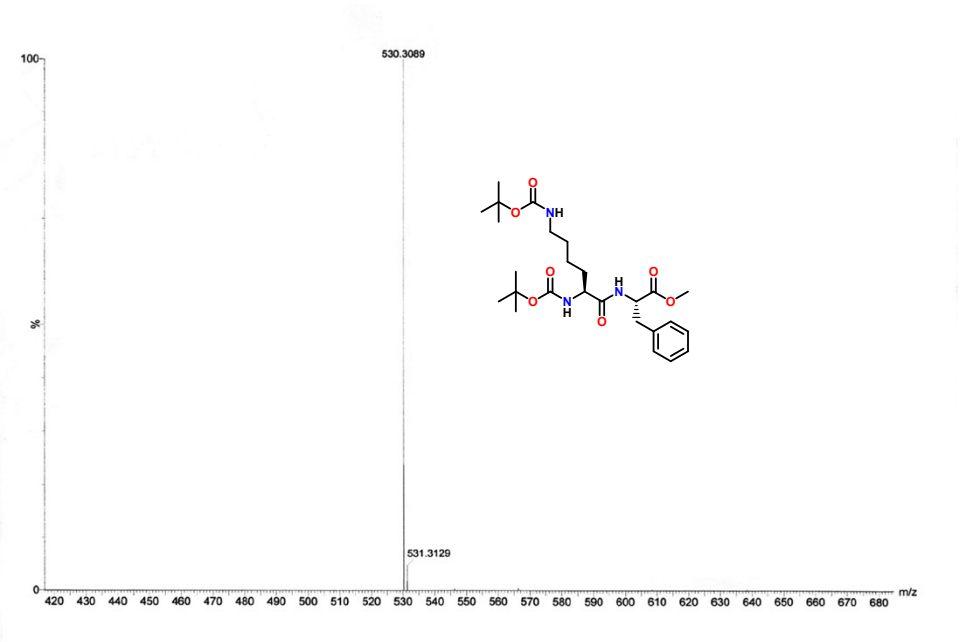

Fig. S3 HRMS spectra of B_2KFO

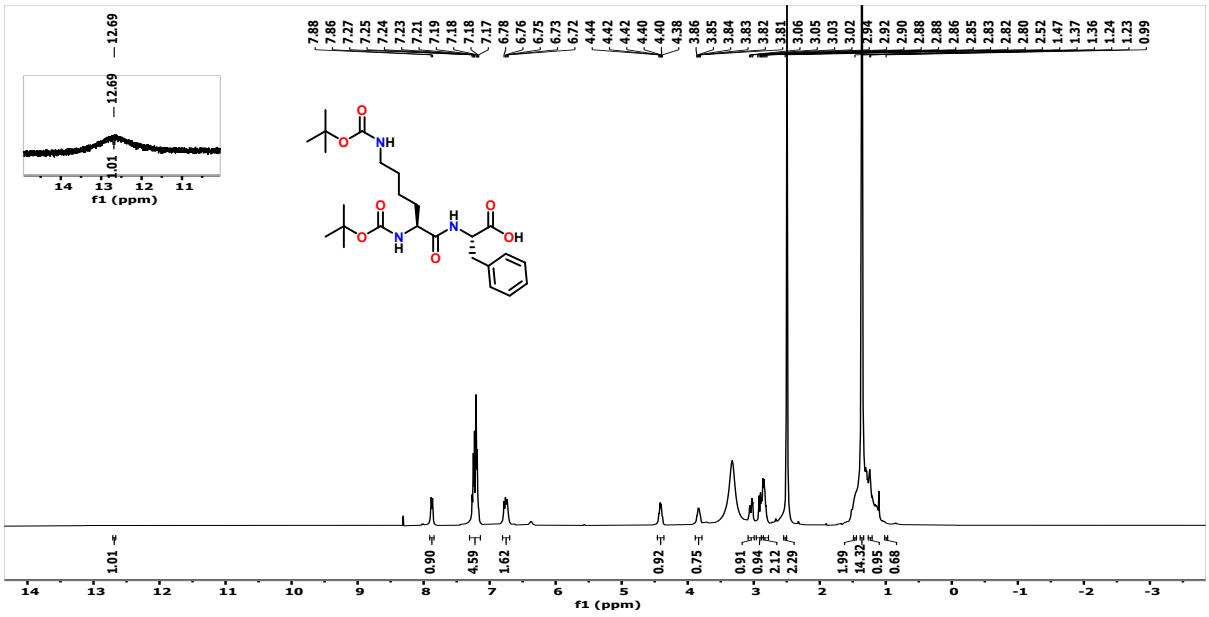

Fig. S4 ^{1}H NMR spectra of B_2KF-OH

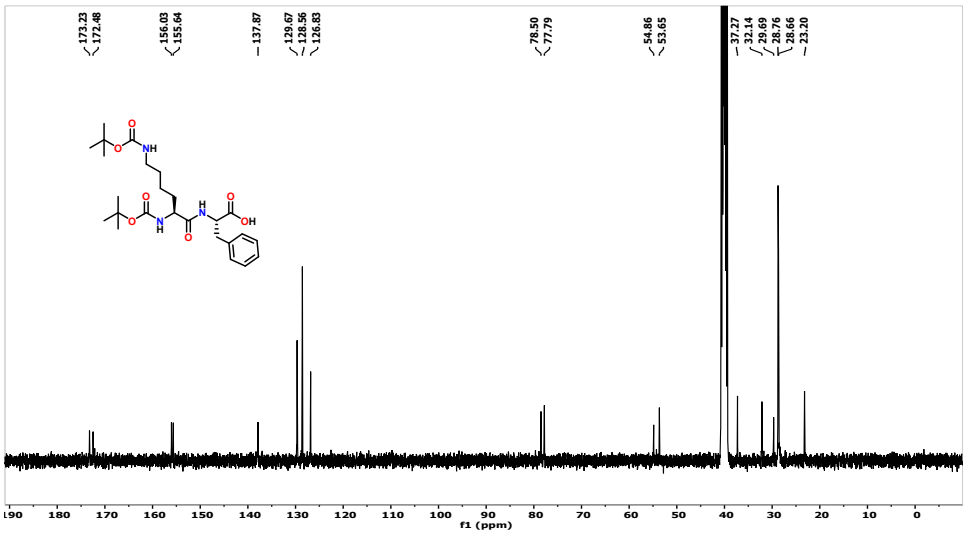

Fig. S5 ^{13}C NMR spectra of B_2KF-OH

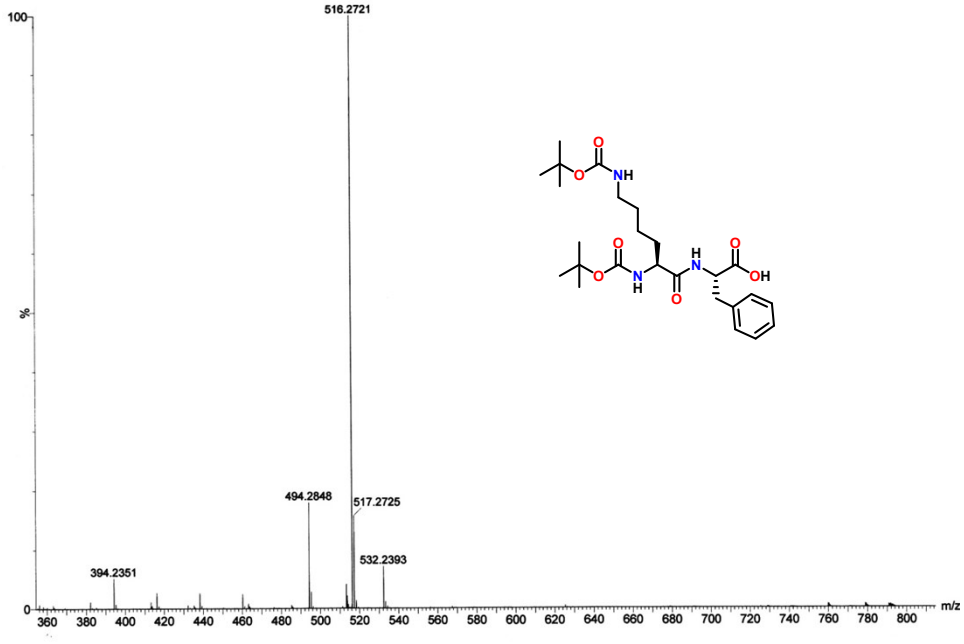

Fig. S6 HRMS spectra of B_2KF-OH

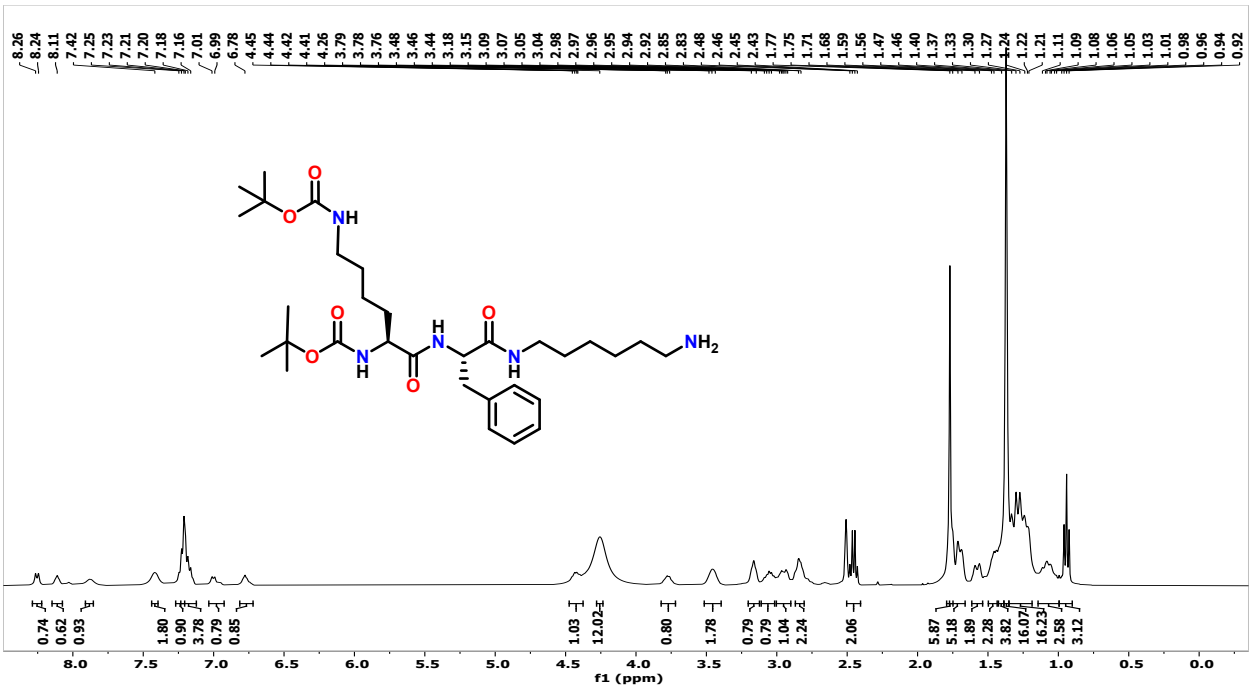

Fig. S7 ^{1}H NMR spectra of B_2KFC_6-NH_2

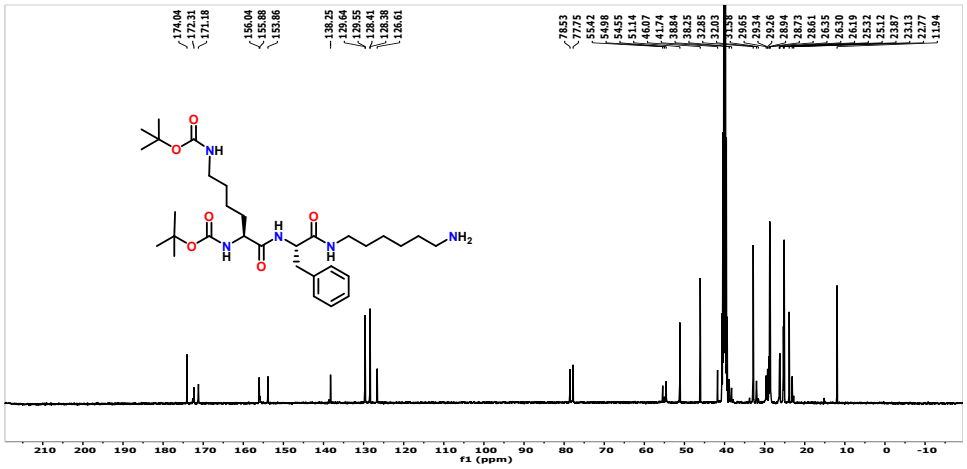

Fig. S8 ^{13}C NMR spectra of B_2KFC_6-NH_2

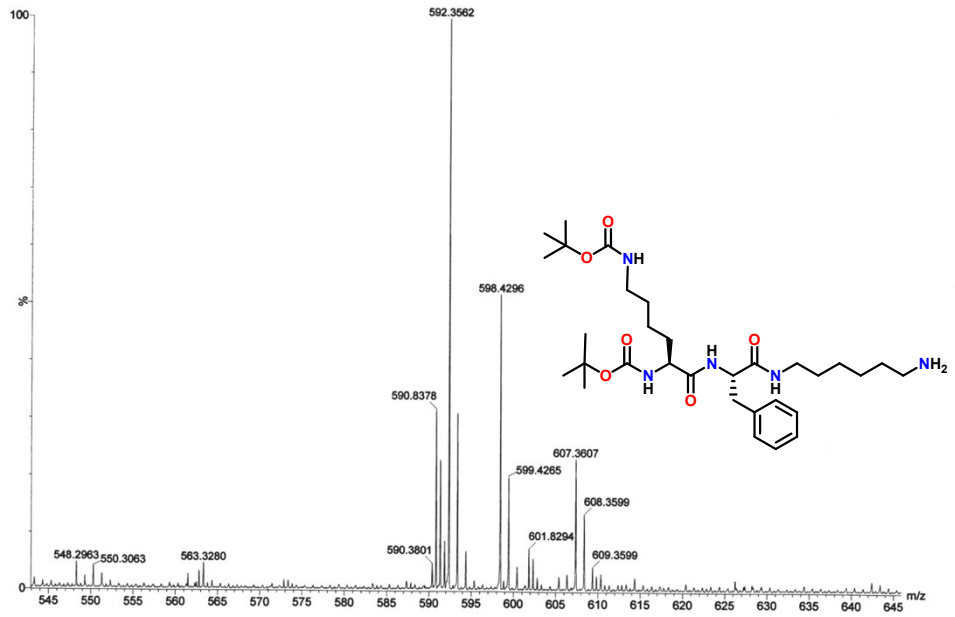

Fig. S9 HRMS spectra of B_2KFC_6-NH_2

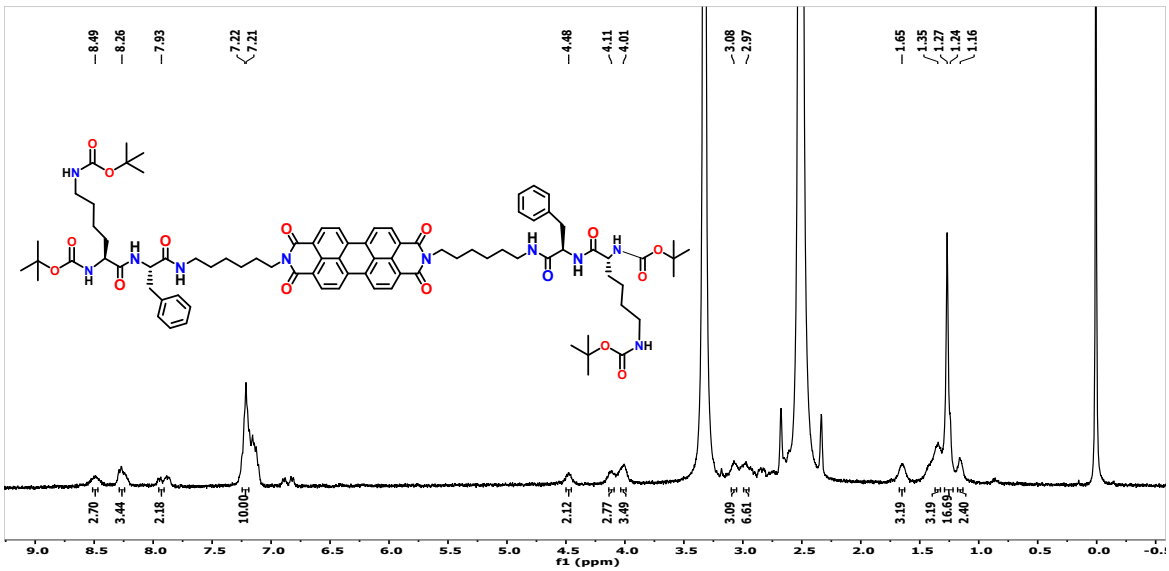

Fig. S10 1H NMR spectra of PBI-$(C_6FKB_2)_2$

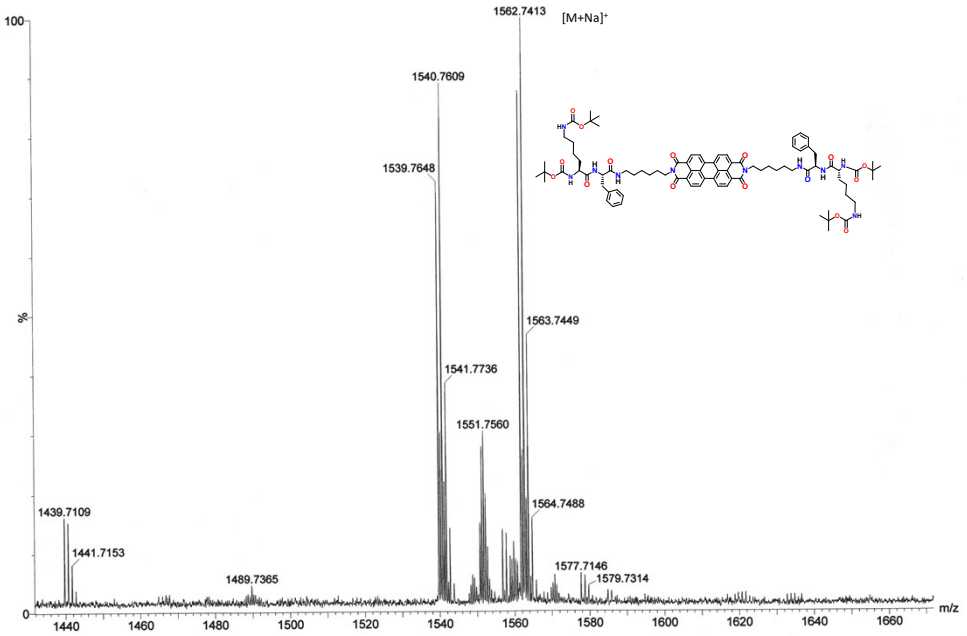

Fig. S11 HRMS spectra of PBI-$(C_6FKB_2)_2$

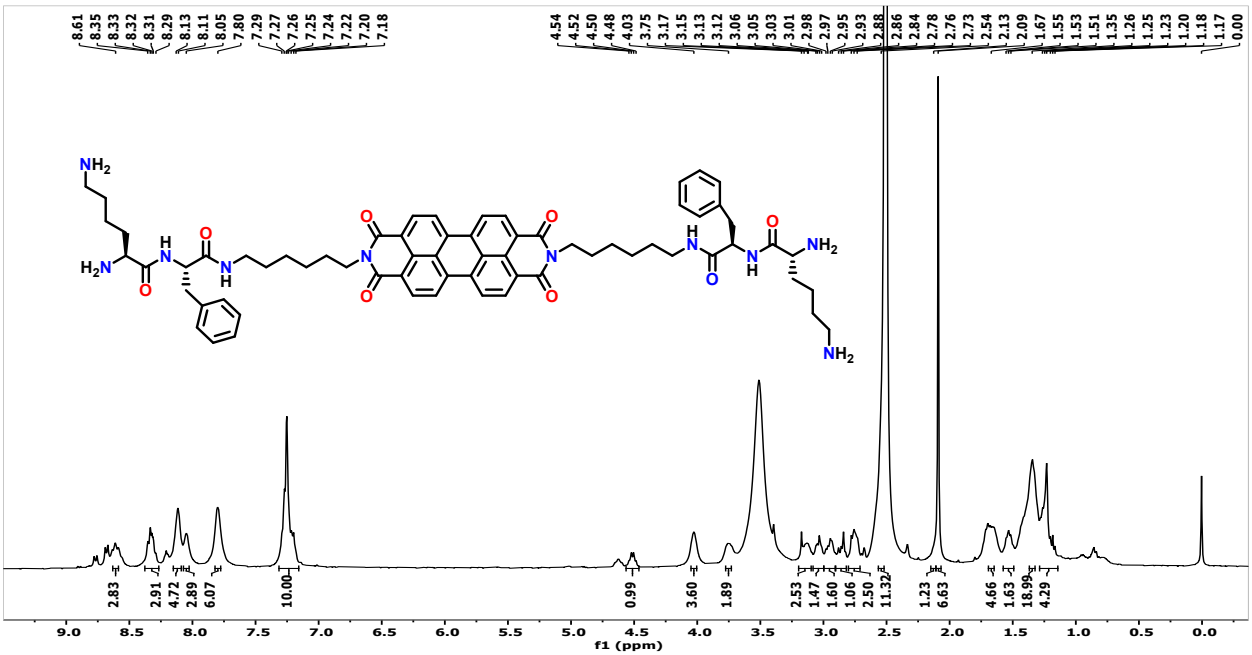

Fig. S12 ^{1}H NMR spectra of PBI-CFK

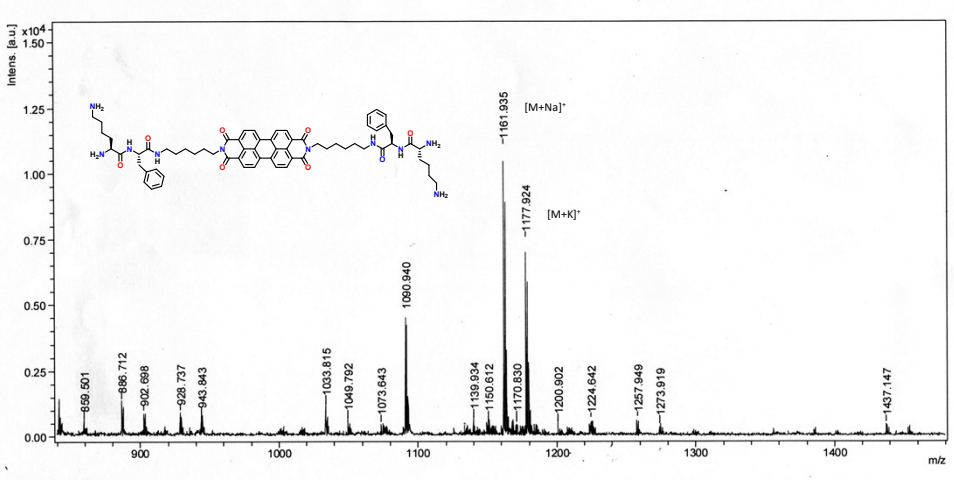

Fig. S13 MALDI-TOF MS spectra of PBI-CFK

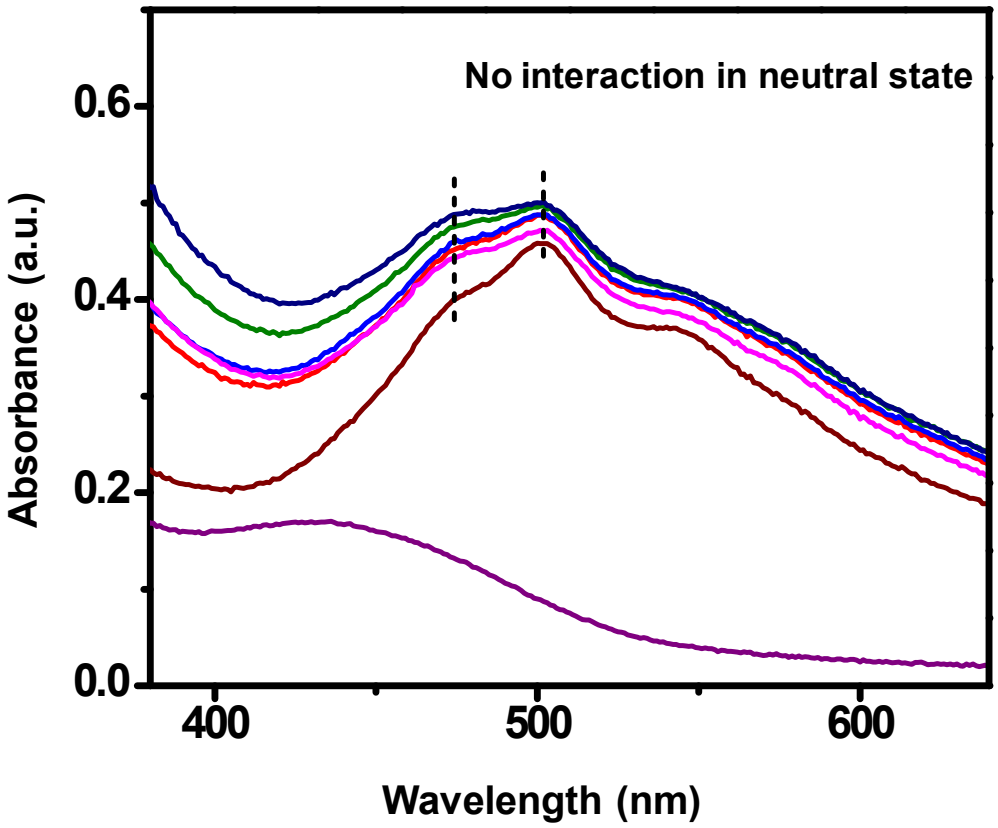

Fig. S14 No interaction of Fc with neutral PBI-CFK-NH_2

Table S1: Changes of average lifetime of the PBI-CFK upon the addition of Fc at different equivalent amount.

Samples	Life time (τ_1/ns)	Relative amplitude (α_1)	Life time (τ_2/ns)	Relative amplitudes (α_2)	Average life time ($<\tau>$/ns)
PBI-CFK (0.05 mg/ml)	1.94089	7.57	4.58505	92.43	4.156228
PBI-CFK+ Fc (0.10 eqv)	1.43847	4.64	4.50937	95.36	4.102882
PBI-CFK+ Fc (0.30 eqv)	1.68107	6.54	4.54297	93.46	4.08778
PBI-CFK+ Fc (0.50 eqv)	0.961389	4.00	4.46526	96.00	3.897599
PBI-CFK+ Fc (0.70 eqv)	1.97382	7.14	4.57383	82.66	3.273825
PBI-CFK+ Fc (1.00 eqv)	2.3232	10.11	4.63604	88.23	3.247974

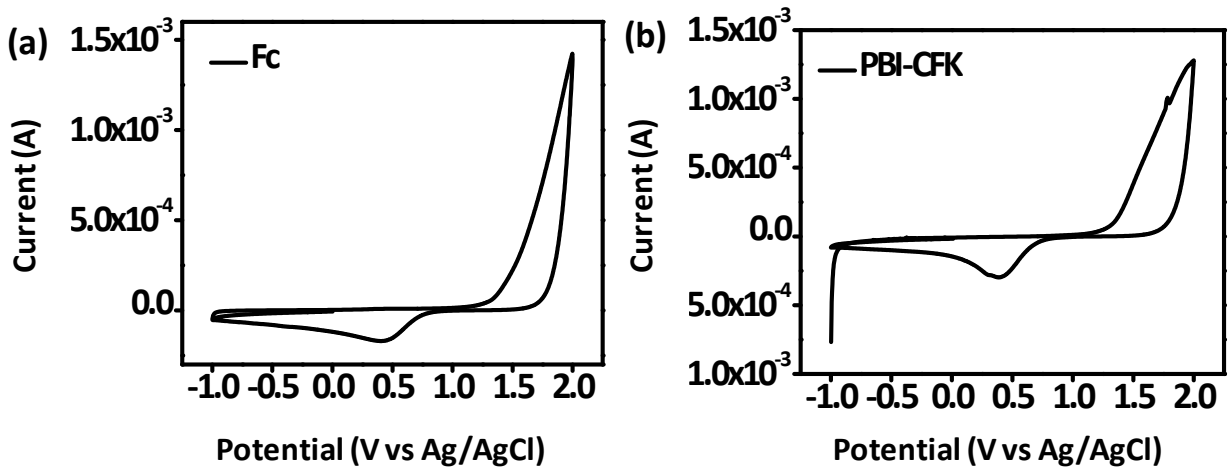

Fig. S15 Cyclic voltamogram of Fc (a) (1.00 equivalent) and PBI-CFK (b) (0.05 mg/ml)

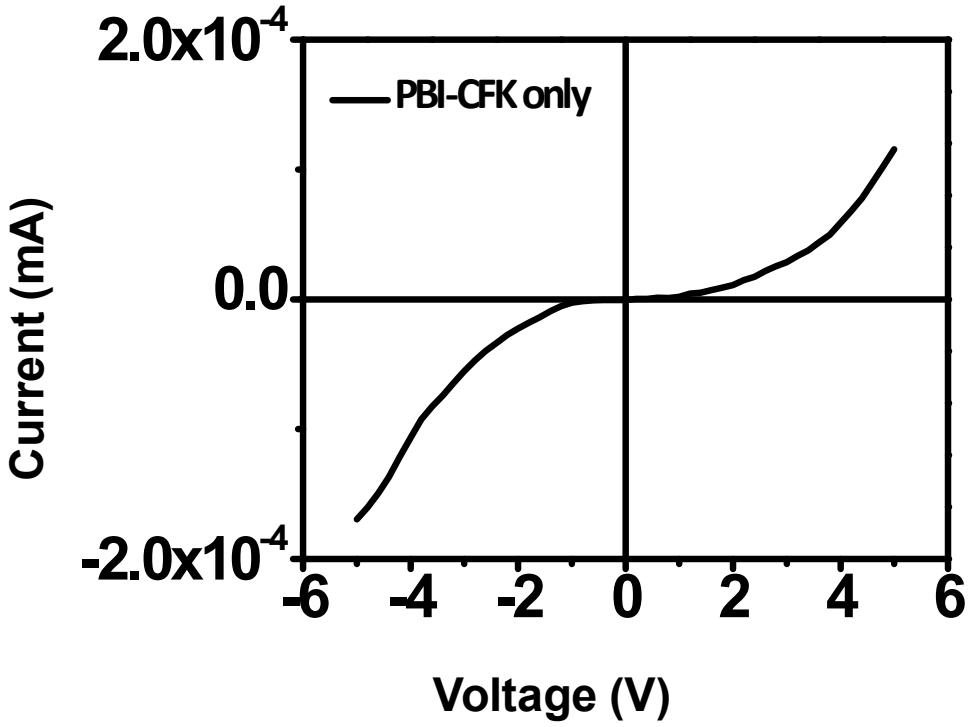

Fig. S16 Current−Voltage (I−V) behavior of PBI-CFK only (Zoomed mode)

Table S2: Responsivity of photocurrent with the addition of Fc to PBI-CFK.

Equivalent amount of Fc in PBI-CFK	Responsivity (R) in µA/W
0	3.11
0.1	5.65
0.3	23.53
0.5	221.42
0.7	603.85
1.0	923.65