Electronic Supplementary Information

Photo-induced electron transfer in a pyrenylcarbazole containing polymer-multiwall carbon nanotube composite

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Synthetic Procedures

Pyrene, methacryloyl chloride, *n*-butyllithium (2.5 M in hexanes), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, tetrabutylammonium hydrogensulfate and anhydrous chlorobenzene were purchased from Aldrich Chemicals Co.. Triethylamine and carbazole were purchased from Merck Chemical Ltd.. Magnesium turnings for Grignards and tetrakis(triphenylphosphine)palladium(0) were purchased from Strem Chemicals Inc. 2,2'-Azobis(isobutyronitrile) (AIBN) was purchased from Hengye Chemical Industry Co. Ltd. *N*-Bromosuccinimide was purchased from Alfa Aesar. Column chromatography was performed using Merck 9385

silica gel 60 (0.040 – 0.063 mm). MWCNT were purchased from NanoLab Inc (length = 5-20 μm, OD = 15 ± 5 nm). AIBN was recrystallized with ethanol before use. DMF and carbon disulfide were distilled over calcium hydride and triethylamine were distilled over potassium hydroxide before use. 12-Bromododecan-1-ol[1], 3-bromocarbazole[2] and 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene **1**[3] were synthesized according to literature procedures.

1-Bromopyrene

The compound was synthesized according to a modified literature procedure.[4] To a 1:1 methanol/diethyl ether solution (430 cm^3) of pyrene, hydrobromic acid (48%, 15.4 cm^3, 0.136 mol) was added. The mixture was cooled to 10 – 15 °C in an ice-bath. Hydrogen peroxide (30%, 12.7 cm^3, 0.124 mol) was added dropwise and the mixture was stirred at room temperature for 1 day. The precipitate was filtered and washed with a small amount of diethyl ether, plenty of water and then a small amount of diethyl ether. Recrystallization of the crude product with ethanol gave a pale yellow solid. Yield: 29.3 g (84.4%). ^{1}H NMR (300 MHz, CDCl3) δ (ppm): 8.45 (d, 1H, J = 9.2 Hz), 8.26 – 8.17 (m, 4H), 8.12 – 8.01 (m, 4H). EIMS (*m/z*): 282.0 [M ^{81}Br]$^+$, 280.0 [M ^{79}Br]$^+$, 201.1 [M - Br]$^+$.

12-(3-bromo-9*H*-carbazol-9-yl)dodecan-1-ol (2)

To an acetone solution (2.2 cm^3) of 3-bromocarbazole (0.500 g, 2.02 mmol), tetrabutylammonium hydrogensulfate (0.021 g, 0.06 mmol), 12-bromododecan-1-ol

(0.872 g, 3.29 mmol) and potassium hydroxide (0.216 g, 3.86 mmol) were added. The mixture was heated under reflux under a nitrogen atmosphere for 1 day. The precipitate was filtered and the filtrate was obtained. The solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel eluting with 3:1 hexane/ethyl acetate as a white solid. Yield: 0.679 g (78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.20 (d, 1H, J = 1.8 Hz), 8.04 (d, 1H, J = 7.7 Hz), 7.53 (dd, 1H, J = 8.7 Hz and 2.0 Hz), 7.47 (dd, 1H, J = 7.0 Hz and 1.1 Hz), 7.40 (d, 1H, J = 8.1 Hz), 7.27 (d, 1H, J = 9.2 Hz), 7.22 (d, 1H, J = 7.9 Hz), 4.27 (t, 2H, J = 7.2 Hz), 3.63 (t, 2H, J = 6.2 Hz), 1.85 (p, 2H, J = 7.1 Hz), 1.56 (p, 2H, J = 7.3 Hz), 1.32 – 1.24 (m, 16H). ^{13}C NMR (100 MHz, CDCl3) δ (ppm): 140.9, 139.2, 128.3, 126.5, 124.7, 123.2, 121.9, 120.7, 119.3, 111.6, 110.3, 109.1, 63.1, 43.3, 33.0, 29.8, 29.7, 29.7, 29.6, 29.6, 29.4, 29.1, 27.4, 26.0. EIMS (*m/z*): 431.2 [M ^{81}Br]$^{+}$, 429.2 [M ^{79}Br]$^{+}$, 260.0 [M ^{81}Br - $(CH_2)_{11}OH$]$^{+}$, 258.0 [M ^{79}Br - $(CH_2)_{11}OH$]$^{+}$.

12-(3-(pyren-1-yl)-9*H*-carbazol-9-yl)dodecan-1-ol (3)

Compound **2** (0.430 g, 1.00 mmol) and 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene **1** (0.394 g, 1.20 mmol) were dissolved in THF (10 cm^3). The mixture was degassed for 50 minutes by purging nitrogen into the solution. Tetrakis(triphenylphosphine)palladium(0) (0.069 g, 0.06 mmol) and 2 M sodium carbonate solution (5 cm^3, 10.0 mmol) purged with nitrogen for 50 minutes were added. The mixture was stirred at 70 °C under a nitrogen atmosphere for 2 days. The crude product was extracted with dichloromethane for 3 times (3 × 30

cm^3). The combined organic layer was washed with water for 3 times (3 × 150 cm^3) and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation. Silica gel column chromatography eluting with 4:1 hexane/ethyl acetate gave a yellow oily liquid as the product. Yield: 0.373 g (68 %). ^{1}H NMR (300 MHz, CDCl3) δ (ppm): 8.35 (d, 1H, J = 1.3 Hz), 8.29 (d, 1H, 9.3 Hz), 8.26 (d, 1H, J = 7.9 Hz), 8.21 – 8.15 (m, 3H), 8.12 (d, 2H, J = 2.6 Hz), 8.10 (d, 1H, J = 2.2 Hz), 8.03 (d, 1H, J = 1.5 Hz), 8.01 – 7.98 (m, 1H), 7.74 (dd, 1H, J = 8.4 Hz and 1.7 Hz), 7.58 (d, 1H, J = 8.4 Hz), 7.51 – 7.46 (m, 2H), 7.28 – 7.23 (m, 1H), 4.40 (t, 2H, J = 7.2 Hz), 3.62 (t, 2H, J = 6.6 Hz), 1.97 (p, 2H, J = 7.4 Hz), 1.53 – 1.23 (m, 18H). ^{13}C NMR (100 MHz, CDCl3) δ (ppm): 141.2, 140.0, 139.0, 132.0, 131.4, 130.5, 129.1, 128.7, 128.5, 127.8, 127.5, 127.4, 126.2, 126.1, 126.1, 125.2, 124.9, 123.1, 122.6, 120.8, 119.2, 109.1, 108.8, 63.3, 43.5, 33.0, 29.9, 29.8, 29.7, 29.3, 27.6, 26.0. EIMS (*m/z*): 551.4 $[M]^+$.

12-(3-(pyren-1-yl)-9*H*-carbazol-9-yl)dodecyl methacrylate (4)

To an anhydrous DMF solution (13 cm^3) of compound **3** (1.282 g, 2.32 mmol) under a nitrogen atmosphere, triethylamine (4.02 cm^3, 28.8 mmol) was added. The mixture was cooled in an ice-bath and methacryloyl chloride (0.43 cm^3, 4.41 mmol) was added dropwise. The mixture was stirred at room temperature under dark for 16 hours. The crude product was poured into water (180 cm^3) and extracted with dichloromethane for 3 times (3 × 30 cm^3). The organic layer was washed with water for 3 times (3 × 150 cm^3) and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel

eluting with 3:1 dichloromethane/ hexane as a pale yellow oily liquid. Yield: 1.20 g (83%). ^{1}H NMR (300 MHz, CDCl3) δ (ppm): 8.35 (d, 1H, J = 1.3 Hz), 8.28 (m, 2H), 8.20 (d, 1H, J = 7.5 Hz), 8.16 (d, 2H, J = 7.1 Hz), 8.13 – 8.10 (m, 3H), 8.04 (d, 1H, J = 1.7 Hz), 8.01 – 8.00 (m, 1H), 7.74 (dd, 1H, J = 8.3 Hz and 1.6 Hz), 7.58 (d, 1H, J = 8.3 Hz), 7.51 – 7.49 (m, 2H), 7.28 – 7.25 (m, 1H), 6.08 (s, 1H), 5.53 (s, 1H), 4.40 (t, 2H, J = 7.2 Hz), 4.13 (t, 2H, J = 6.7 Hz), 1.97 (p, 2H, J = 7.1 Hz), 1.93 (s, 3H), 1.66 (p, 2H, J = 7.0 Hz), 1.52 – 1.28 (m, 16H). ^{13}C NMR (100 MHz, CDCl3) δ (ppm): 157.8, 141.2, 140.0, 139.0, 136.8, 132.0, 131.8, 131.4, 130.5, 129.1, 128.7, 128.5, 127.8, 127.5, 127.4, 126.2, 126.1, 126.0, 125.5, 125.4, 125.3, 125.2, 124.9, 123.3, 123.1, 122.6, 120.8, 119.2, 109.1, 108.8, 65.1, 43.5, 29.9, 29.8, 29.7, 29.5, 29.4, 28.9, 27.7, 26.3, 18.6.

Dithiobenzodisulfide

The compound was prepared by a modified literature procedure.[5] Phenylmagnesium bromide was first prepared by adding bromobenzene (10.7 cm^3, 0.102 mol) dropwise to magnesium turnings (2.60 g, 0.107 mol) in stirred anhydrous THF (40 cm^3) under a nitrogen atmosphere. The mixture was heated under reflux for 90 minutes. After cooling to 0 °C, carbon disulfide (6.1 cm^3, 0.102 mol) was added and the mixture was stirred for 30 minutes at room temperature. Water was added slowly to quench the excess Grignard reagent. The precipitate was filtered and the filtrate was obtained. After the removal of solvent by distillation, concentrated hydrochloric acid was added to the solution until the solution changed from red to purple. The solution was extracted with dichloromethane for 3 times (3 × 30 cm^3). The combined organic layer was washed

with water for 3 times (3 × 150 cm^3) and dried over anhydrous magnesium sulfate. Remove the solvent yielded purple oil. The oil was dissolved in ethanol (15 cm^3), and then DMSO (3.6 cm^3) and iodine (5 mg, 0.02 mmol) was added. The mixture was put into a freezer overnight. The crude product was filtered and recrystallization with ethanol gave a purple solid. Yield: 5.57 g (35.7%). ^{1}H NMR (300 MHz, CDCl3) δ (ppm): 8.09 (d, 4H, J = 7.4 Hz), 7.61 (t, 2H, J = 7.5 Hz), 7.45 (t, 4H, J = 7.7 Hz).

2-Cyanoprop-2-yl Dithiobenzoate (5)

The chain transfer agent was synthesized by a modified literature procedure.[6] Ethyl acetate (16 cm^3) was degassed by purging nitrogen into the solution for 30 minutes. AIBN (1.34 g, 8.12 mmol) and dithiobenzodisulfide (1.00 g, 3.26 mmol) were added. The mixture was heated under reflux for 18 hours under a nitrogen atmosphere. Removal of the solvent and purification by silica gel column chromatography eluting with 3:1 hexane/ ethyl acetate gave a red oily liquid as the product. Yield: 0.68 g (47.1%). ^{1}H NMR (300 MHz, CDCl3) δ (ppm): 7.92 (d, 2H, J = 9.5 Hz), 7.56 (t, 1H, J = 7.4 Hz), 7.40 (t, 2H, J = 7.8 Hz), 1.94 (s, 6H)

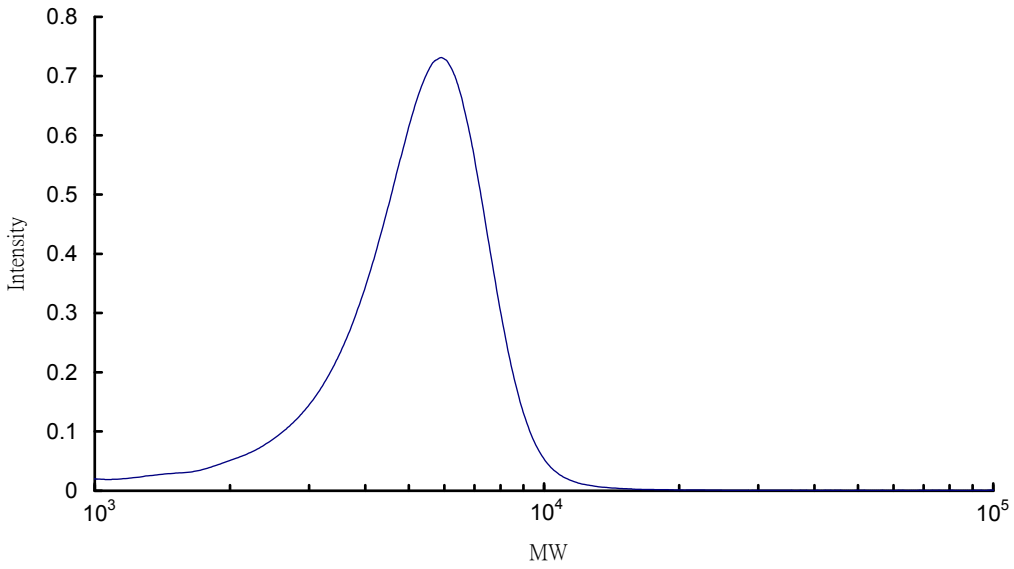

Fig. S1. Gel permeation chromatogram of **PCP**.

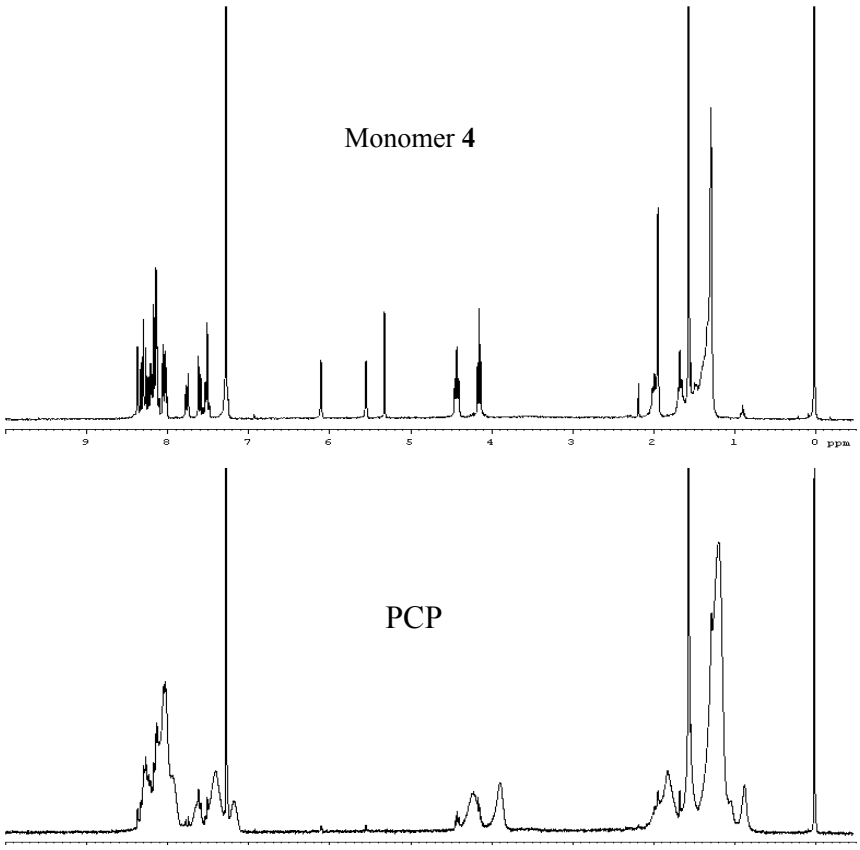

Fig. S2. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of monomer **4** and **PCP**.

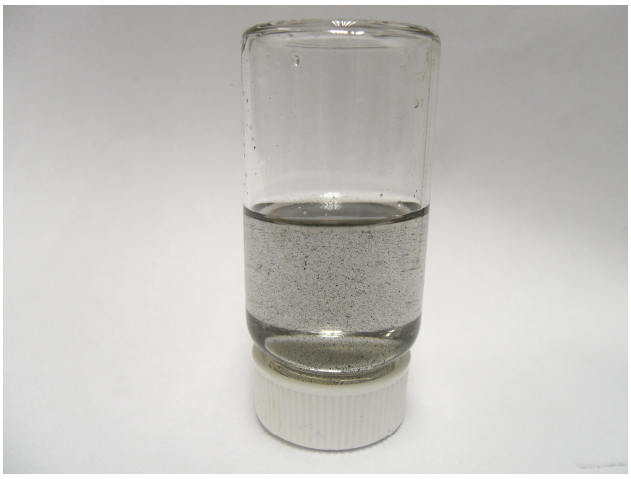

Fig. S3. Image of MWCNT dispersed in chloroform.

Table S1 Standard orientation of pyrenylcarbazole-including side chain of **PCP** by TDDFT calculations:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-8.925590	-2.755618	2.874739
2	6	0	-8.104050	-2.001716	2.024086
3	6	0	-8.610640	-1.579387	0.760292
4	6	0	-9.944381	-1.923904	0.385626
5	6	0	-10.727226	-2.681682	1.268298
6	6	0	-10.221108	-3.092016	2.497371
7	6	0	-6.769010	-1.621325	2.382482
8	6	0	-5.984852	-0.898095	1.541034
9	6	0	-6.449488	-0.480201	0.245471
10	6	0	-7.790707	-0.813612	-0.122585
11	6	0	-8.322686	-0.378485	-1.372018
12	6	0	-7.511651	0.388045	-2.217689
13	6	0	-6.208184	0.700190	-1.860218
14	6	0	-5.648181	0.269812	-0.650560
15	6	0	-10.440711	-1.478066	-0.885331
16	6	0	-9.667397	-0.738299	-1.720983
17	6	0	-4.227067	0.612249	-0.361159
18	6	0	-3.813472	1.946716	-0.345672
19	6	0	-2.471784	2.260980	-0.124177
20	6	0	-1.530297	1.219968	0.078477
21	6	0	-1.924149	-0.119454	0.056175
22	6	0	-3.266957	-0.403007	-0.159305
23	7	0	-0.274527	1.773490	0.286915
24	6	0	-0.382553	3.157256	0.206657
25	6	0	-1.736546	3.504353	-0.039018
26	6	0	-2.094996	4.850857	-0.142783
27	6	0	-1.113907	5.825693	-0.007251
28	6	0	0.221443	5.466719	0.230418
29	6	0	0.606337	4.134477	0.338381
30	6	0	0.960016	1.028893	0.475733
31	6	0	1.687753	0.697467	-0.834948
32	6	0	2.983794	-0.087815	-0.607486
33	6	0	3.721803	-0.426693	-1.907810
34	6	0	5.019784	-1.213164	-1.690304
35	6	0	5.746702	-1.551573	-2.998457

36	6	0	7.015683	-2.401832	-2.829988
37	6	0	8.174911	-1.694781	-2.115202
38	6	0	9.435693	-2.564167	-2.022107
39	6	0	10.651776	-1.872792	-1.386158
40	6	0	10.475808	-1.525285	0.097592
41	6	0	11.733624	-0.922103	0.702007
42	8	0	11.444852	-0.616845	2.078466
43	6	0	12.370992	-0.059833	2.906722
44	8	0	12.062588	0.173360	4.042638
45	6	0	13.744654	0.233161	2.336813
46	1	0	-1.379246	6.873480	-0.085833
47	1	0	0.971687	6.243007	0.330876
48	1	0	1.642480	3.873719	0.517669
49	1	0	-3.126150	5.132117	-0.326282
50	1	0	-1.211785	-0.924760	0.190405
51	1	0	-3.586040	-1.438175	-0.196845
52	1	0	-4.543068	2.735388	-0.493379
53	1	0	-5.589102	1.270020	-2.543990
54	1	0	-4.987843	-0.611688	1.848921
55	1	0	-7.907264	0.726152	-3.169766
56	1	0	-6.392993	-1.916515	3.356727
57	1	0	-10.056609	-0.403568	-2.677012
58	1	0	-8.538322	-3.074113	3.836800
59	1	0	-11.739871	-2.945016	0.981619
60	1	0	-11.455039	-1.743219	-1.164795
61	1	0	-10.842408	-3.676104	3.167138
62	1	0	0.720560	0.110179	1.018702
63	1	0	1.610157	1.612946	1.133420
64	1	0	1.905766	1.630648	-1.365580
65	1	0	1.012945	0.124455	-1.480202
66	1	0	2.758290	-1.016784	-0.067816
67	1	0	3.650334	0.488977	0.046816
68	1	0	3.054756	-1.002539	-2.561746
69	1	0	3.947209	0.502164	-2.446899
70	1	0	4.793355	-2.144464	-1.154683
71	1	0	5.679418	-0.635813	-1.032148
72	1	0	6.001742	-0.621491	-3.522864
73	1	0	5.051912	-2.087702	-3.655999
74	1	0	6.763204	-3.322059	-2.287020
75	1	0	7.358161	-2.720976	-3.821725
76	1	0	8.416077	-0.767591	-2.652472
77	1	0	7.859483	-1.394514	-1.111221
78	1	0	9.711780	-2.893055	-3.030933
79	1	0	9.205777	-3.477341	-1.458428

80	1	0	11.523337	-2.529289	-1.498052
81	1	0	10.883220	-0.960678	-1.951547
82	1	0	9.657050	-0.814243	0.236881
83	1	0	10.213563	-2.424352	0.665285
84	1	0	12.015962	-0.009253	0.165928
85	1	0	12.566908	-1.630677	0.640524
86	1	0	14.226718	-0.677110	1.971400
87	1	0	13.686477	0.933611	1.499831
88	1	0	14.350484	0.668100	3.128086

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